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PATENT APPLICATION

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re A	Application of:)	
TAKE	O TSUKAMOTO	:	Examiner: NYA
Application No.: 09/941,595 ;		:	Group Art Unit: 2879
Filed:	August 30, 2001)	
For:	ELECTRON-EMITTING DEVICE, ELECTRON SOURCE AND IMAGE-FORMING APPARATUS, AND METHOD FOR MANUFAC- TURING ELECTRON EMITTING DEVICE	;) :	November 29, 2001

Commissioner for Patents Washington, D.C. 20231

INFORMATION DISCLOSURE STATEMENT

Sir:

In compliance with the duty of disclosure under 37 C.F.R. § 1.56 and in accordance with the practice under 37 C.F.R. §§ 1.97 and 1.98, the Examiner's attention is directed to the documents listed on the enclosed Form PTO-1449. Copies of the listed documents are also enclosed.

For the concise explanation of relevance for the non-English documents, the Examiner is respectfully referred to the English Abstracts attached thereto, and for document 11-194134, the Examiner is also respectfully referred to EP 0 913 508 A2, cited in the Information Disclosure Statement filed on August 30, 2001.

The Examiner's attention is also directed to the following U.S. applications:

APPLICATION NO.	FILING DATE	GROUP ART UNIT
09/191,342	11/13/98	2879
09/941,780	8/30/01	2817
09/940,642	8/29/01	2879
09/940,643	8/29/01	2852
08/781,206	1/10/97	2879

A copy of each cited Application is enclosed.

CONCLUSION

It is respectfully requested that the above information be considered by the Examiner and that a copy of the enclosed Form PTO-1449 be returned indicating that such information has been considered.

Applicant's undersigned attorney may be reached in our New York office by telephone at (212) 218-2100. All correspondence should continue to be directed to our address given below.

Respectfully submitted,

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GAU-2479

ELECTRON-EMITTING DEVICE

AND PRODUCTION METHOD THEREOF



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BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to an electronemitting device and a production method thereof and,
more particularly, to an electron-emitting device
having a lower electrode, an insulating layer having
pores, and an upper electrode stacked in this order on
a substrate, and a method for producing the electronemitting device.

Related Background Art

The conventionally known electron-emitting

devices are generally classified under two kinds,
thermionic emission devices and cold cathode emission
devices. The cold cathode emission devices include
field emission type (FE type) devices,
metal/insulator/metal type (MIN type) devices, surface
conduction electron-emitting devices, and so on.

The FE type devices are disclosed, for example, in W. P. Dyke & W. W. Dolan, "Field emission," Advance in Electron Physics, 8, 89 (1956) or in C. A. Spindt, "PHYSICAL Properties of thin-film field emission cathodes with molybdenum cones," J. Appl. Phys., 47,

25 cathodes with molybdenum cones," J. Appl. Phys., 47,

The tip of an electron-emitting body of the

field emission type electron-emitting devices is one called a cone having the three-dimensionally sharp-pointed shape and an electron beam is emitted from the tip of the cone by placing a strong electric field between a gate electrode with an aperture, disposed above the cone, and an electron-emitting region.

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In order to overcome the problem in the production method of the above field emission devices, which is the need for complicated steps and expensive apparatus for forming a recessed portion for formation of the electron-emitting region, Japanese Laid-open Patent Applications No. 5-198252 and No. 5-211029 describe examples in which holes of an anodic oxide film of aluminum are used as apertures of the gate electrode and in which electron-emitting regions are formed in the holes of the anodic oxide film. These conventional examples will be described referring to Figs. 32 and 33.

Fig. 32 is a sectional view of the electronemitting device in Japanese Laid-open Patent
Application No. 5-198252. Fig. 33 is a sectional view
of the electron-emitting device in Japanese Laid-open
Patent Application No. 5-211029. In Fig. 32, reference
numeral 161 designates an insulating substrate, 162 an
electroconductive layer, 163 an insulating film, 164
through holes, 165 the gate electrode, and 166
cathodes. The insulating film 163 is the anodic oxide

film of aluminum and the tip of the cathodes 166 is of the cone shape similar to that of the electron-emitting body of the field emission devices. In Fig. 33, reference numeral 171 designates a metal layer, 172 the Al anodic oxide film, 172a micropores, and 173 cylindrical electrodes. The application describes that in Fig. 33 the distance can be made constant between the cylindrical electrodes 173 and the gate electrode or between the needlelike electrodes and the anode electrode, so as to make electron emission efficiency constant.

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The MIM type devices are disclosed, for example, in C. A. Mead, "Operation of Tunnel-Emission Devices," J. Appl. Phys., 32, 646 (1961).

Recent researches on the MIM type are seen in Toshiaki Kusunoki, "Fluctuation-free electron emission from non-formed metal-insulator-metal (MIM) cathodes fabricated by low current anodic oxidation," Jpn. J. Appl. Phys. vol. 32 (1993) pp L1695, Mutsumi Suzuki et al., "An MIM cathode array for cathode luminescent displays," IDW '96 (1996) p529, and so on.

An MIM type electron-emitting device according to Kusunoki or Suzuki et al. described above will be described referring to Fig. 34. Fig. 34 is a schematic sectional view of the MIM type electron-emitting device. In the same figure, reference numeral 1 denotes a substrate, 2 a lower electrode, 3 an

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insulating layer, and 4 an upper electrode. electron-emitting device is made by a production method for first forming SiO, on the Si substrate by sputtering, depositing Al as the lower electrode, further forming an anodic oxide film of high quality in the thickness of 5.5 nm while controlling oxidation rates, using ethylene glycol and tartaric acid, and thereafter forming Au of the upper electrode in the thickness of 9 nm. It is described that good electron emission characteristics were achieved by applying voltage between the anode of the upper electrode and the cathode of the lower electrode thus formed. Specifically, according to Kusunoki et al., negative resistance does not appear in the device current flowing against the voltage applied to the device. "negative resistance" herein is a phenomenon in which the device current decreases as the device voltage increases. In addition, fluctuation does not occur in the emission current. Here, the "fluctuation" means temporal change of the emission current. It is also described that dependence of the emission current on the device voltage varies depending upon the thickness of the insulating layer and that the thicker the insulating layer, the higher the device voltage that has to be applied. It is further described that with anodic oxide films made at high oxidation rates, the negative resistance appears in the electron emission

characteristics and the fluctuation occurs large.

An example of the surface conduction electronemitting device with improved electron emission characteristics is described in Japanese Laid-open Patent Application No. 9-82214. This will be described referring to Figs. 35A and 35B. In the figures, reference numeral 191 denotes a substrate, 192 an electron-emitting region, 193 an electroconductive film, 194 a cathode device electrode, 195 an anode device electrode, 196 a fissure, and 197 a field correcting electrode. In the surface conduction electron-emitting device of this example, electrons emitted move in an electric field established by the cathode and the anode and a singular point of the electric field above the anode device electrode affects the ratio of electrons reaching the anode electrode, provided to sandwich a vacuum with the electron emitting element i.e., the electron emission efficiency. This device is an example in which the field correcting electrode is provided outside the device electrodes in order to improve the electron emission efficiency.

SUMMARY OF THE INVENTION

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According to the studies by Spindt et al., the conventional FE type electron-emitting devices, however, had a problem of a spread of the electron

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beam, which was hindrance against enhancement of In the example of application of the holes definition. of the anodic oxide film to the apertures of the gate electrode, there remained a problem of poor repeatability in formation of the cone of the electron-In the example in which the electronemitting region. emitting regions were formed in the cylindrical shape, there also arose problems of poor repeatability of the electron emission characteristics and high driving voltage. In the surface conduction electron-emitting device provided with the correcting electrode, the electron emission efficiency was increased, but the potential of the correcting electrode was high, which was a problem in driving.

In the conventional MIM type electron-emitting devices, first, the thickness of the insulating layer was thin, several nm, and the thickness greatly affected the electron emission characteristics. In an electron source equipped with many devices, variations in the thickness of the insulating layer are directly bound to variations in the emission current, so that control of variations is difficult. When an image pickup device or an image forming device is constructed using the electron source, there will arise a problem of degradation of image quality. Second, the quality of the insulating layer did not affect only the electron emission characteristics, but also affected

the device current. In the case of the electron source equipped with many devices, variations in the quality of the insulating layer are directly bound to variations in the emission current. Particularly, in the case of a large area, control of variations is difficult. In the image pickup device or the image forming device using the electron source, there will arise the problem of degradation of image quality. Third, repeatability was poor as to occurrence of the negative resistance and occurrence of the fluctuation of the device current and control thereof was difficult.

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In the conventional surface conduction electron-emitting device provided with the correcting electrode, the electron emission efficiency was increased, but the potential of the correcting electrode was high, which was the problem in driving.

An object of the present invention is thus to provide an electron-emitting device having stable electron emission characteristics with less variation that can achieve high electron emission efficiency, high definition, and low driving voltage.

For accomplishing the above object, the present invention provides an electron-emitting device comprising a lower electrode, an insulating layer having a pore, and an upper electrode stacked in this order on a substrate, wherein a carbon deposit is

provided in the pore.

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The present invention also provides an electron-emitting device comprising a lower electrode, an insulating layer having a pore, and an upper electrode stacked in this order on a substrate, wherein an electron-emitting region is provided in the pore, the electron-emitting region is comprised of a small gap between the lower electrode and the upper electrode, and the small gap is formed by a rim-shape electroconductive body formed along an inner wall of the pore, and the upper electrode.

The present invention further provides an electron-emitting device comprising a lower electrode, an insulating layer having a pore, and an upper electrode stacked in this order on a substrate, wherein an electron-emitting body is provided in the pore, and

where when a thickness of the upper electrode is t, a length of the pore is L, and a mean free path of electron transmission of the upper electrode is λ , they satisfy the following condition: $0.5 \times L \le t < 2\lambda$.

The present invention also provides an electron-emitting device having a lower electrode, an insulating layer having a pore, and an upper electrode stacked in this order on a substrate, the electron-emitting device having an electron-emitting region in the pore,

wherein the electron-emitting region is

comprised of a small gap between the lower electrode and the upper electrode and wherein a distance from the small gap to a top surface of the upper electrode is not more than 200 nm.

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The present invention further provides a production method for producing an electron-emitting device comprising a lower electrode, an insulating layer having a pore, and an upper electrode stacked in this order on a substrate, the electron-emitting device having a carbon deposit in the pore, the production method comprising a step of forming the lower electrode of a metal or a semiconductor on the substrate, a step of forming an anodic oxide layer on a surface of the lower electrode, a step of producing the carbon deposit in the pore of the anodic oxide layer by applying a voltage under existence of an organic material, and a step of forming the upper electrode.

The present invention further provides a production method for producing an electron-emitting device comprising a lower electrode, an insulating layer having a pore, and an upper electrode stacked in this order on a substrate, the electron-emitting device having a carbon deposit in the pore, the production method comprising a step of forming the lower electrode of a metal or a semiconductor on the substrate, a step of forming an anodic oxide layer on a surface of the lower electrode, a step of forming the upper electrode

on the lower electrode after formation of the anodic oxide layer, and a step of producing a carbon deposit in the pore of the anodic oxide layer by applying a voltage to the upper electrode and the lower electrode under existence of an organic material.

In the electron-emitting devices of the present invention, the holes are formed in the porous structure in the insulating layer such as the oxide film formed by anodic oxidation, at least the carbon deposit being the electron-emitting body is formed in the holes of the porous structure, and the gap is provided between the lower electrode and the upper electrode; therefore, with application of the voltage between the lower electrode and the upper electrode so as to keep the upper electrode at a higher potential, the electrons injected from the lower electrode tunnel through the gap between the carbon, formed on the lower electrode, and the upper electrode into a vacuum, whereby the electrons are emitted.

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BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1A and Fig. 1B are a sectional view and a perspective view of an electron-emitting device in the first embodiment of the present invention;

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Fig. 2A, Fig. 2B, Fig. 2C, and Fig. 2D are sectional views for explaining structures of the electron-emitting device of the first embodiment;

- Fig. 3 is a flowchart of a process for producing the electron-emitting device of the first embodiment;
- Fig. 4 is a sectional view of an anodic

 oxidation system used in production of the electronemitting device;
 - Fig. 5 is a sectional view of a vacuum process system used in production of the electron-emitting device;
- 10 Fig. 6A and Fig. 6B are waveform diagrams of voltage pulses applied in a step of forming carbon in the pores of the anodic oxide layer;

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- Fig. 7A and Fig. 7B are a plan view and a sectional view of electron-emitting devices in Example 1 of the first embodiment;
- Fig. 8A and Fig. 8B are graphs to show characteristics of electron-emitting devices in Example 1 of the first embodiment;
- Fig. 9A and Fig. 9B are a sectional view and a
 20 plan view of an image pickup device in Example 3 of the
 first embodiment;
 - Fig. 10A and Fig. 10B are a sectional view and a plan view of a display device in Example 4 of the first embodiment;
- 25 Fig. 11A and Fig. 11B are a sectional view and a perspective view of an electron-emitting device in the second embodiment of the present invention;

Fig. 12A, Fig. 12B, Fig. 12C, and Fig. 12D are sectional views for explaining structures of the electron-emitting device of the second embodiment;

Fig. 13 is a sectional view for explaining the principle of operation of the electron-emitting device in the second embodiment;

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Fig. 14 is a flowchart of a process for producing the electron-emitting device of the second embodiment;

Fig. 15 is a sectional view of another anodic oxidation system used in production of the electron-emitting device;

Fig. 16 is a sectional view of a columnar metal forming system used in production of the electron-emitting device;

Fig. 17A and Fig. 17B are sectional views for explaining sectional configurations of the electron-emitting device of the second embodiment;

Fig. 18 is a graph to show the relation between electron emission efficiency and thickness of the upper electrode in the electron-emitting device of the second embodiment;

Fig. 19 is a graph to show the relation between electron emission efficiency and diameter of aperture in the electron-emitting device of the second embodiment;

Fig. 20A and Fig. 20B are a sectional view and

a perspective view of an electron-emitting device in the third embodiment of the present invention;

Fig. 21A, Fig. 21B, Fig. 21C, and Fig. 21D are sectional views for explaining structures of the electron-emitting device of the third embodiment;

Fig. 22A and Fig. 22B are sectional views for explaining other structures of the electron-emitting device of the third embodiment;

Fig. 23 is a flowchart of a process for producing the electron-emitting device of the third embodiment;

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Fig. 24 is a graph to show the relation between electron emission current and thickness of the upper electrode in the third embodiment;

Fig. 25A and Fig. 25B are a sectional view and a perspective view of an electron-emitting device in the fourth embodiment of the present invention;

Fig. 26A and Fig. 26B are sectional views for explaining structures of the electron-emitting device of the fourth embodiment;

Fig. 27 is a sectional view for explaining the principle of operation of the electron-emitting device in the fourth embodiment;

Fig. 28 is a flowchart of a process for producing the electron-emitting device of the fourth embodiment;

Fig. 29A and Fig. 29B are sectional views for

explaining configurations of the electron-emitting device of the fourth embodiment;

Fig. 30 is a graph to show the relation between electron emission efficiency and thickness of the upper electrode in the electron-emitting device of the fourth embodiment;

Fig. 31 is a graph to show the relation between electron emission efficiency and diameter of aperture in the electron-emitting device of the fourth embodiment;

Fig. 32 is a sectional view of a conventional FE type electron-emitting device;

Fig. 33 is a sectional view of another conventional FE type electron-emitting device;

Fig. 34 is a sectional view of a conventional MIM type electron-emitting device; and

Fig. 35A and Fig. 35B are a plan view and a sectional view of a conventional surface conduction electron-emitting device.

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DESCRIPTION OF THE PREFERRED EMBODIMENTS

Embodiments of the present invention will be described by reference to the drawings.

[First Embodiment]

25 Fig. 1A is a schematic, sectional view to show an example of the electron-emitting device according to the present invention. Fig. 1B is a partly enlarged,

schematic view of part A of Fig. 1A. In Fig. 1A, numeral 1 designates a substrate, 2 a lower electrode, 3 an anodic oxide layer, and 4 an upper electrode. In Fig. 1B, numeral 5 represents pores in the porous structure, and 6 carbon electrically connected to the lower electrode.

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The substrate 1 to be employed herein can be selected from quartz glass, glass with a decreased content of impurity such as Na, soda lime glass, a glass substrate obtained by depositing SiO₂ on soda lime glass by sputtering or the like, ceramics such as alumina, an Si substrate, an Si substrate with a deposited layer of SiO₂, and so on. Particularly, when the substrate 1 is a semiconductor substrate, a driver or the like for driving the electron-emitting device can also be mounted simultaneously.

The lower electrode 2 is selected from metals, such as Al, Ta, Nb, Ti, Zr, Hf, or Si, and semiconductors that can undergo anodic oxidation. The thickness of the lower electrode 2 is properly determined according to the thickness of the anodic oxide layer, the electrical resistance of the lower electrode, and so on.

The anodic oxide layer 3 is formed by anodic oxidation of the lower electrode in part. In the anodic oxide layer 3 there exist regular or irregular pores 5. This will also be called porous structure in

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the present specification. The regular or irregular pores 5 can be formed by selecting anodic oxidation conditions including a composition of an anodic oxidation bath, the temperature of the bath, the voltage, the time, etc., according to the material for the lower electrode 2. Preferably, the regular pores are selected. Diameters of the pores range from several ten nm to several hundred nm and depths thereof from several ten nm to several hundred nm. The density of the pores is 10^8 to 10^{12} pores/cm² and corresponds to the density of electron-emitting points. electron-emitting point indicates a small area where electrons are emitted. In each pore 5, carbon 6, which is an electron-emitting body electrically connected to the lower electrode 2, is deposited on the wall of hole or is formed in a pole shape filling a part of each The carbon may also be formed in the similar fashion from the side of the upper electrode 4.

There is a gap created between the carbon, formed on the lower electrode 2, and the upper electrode or, in the case where the carbon is also formed from the side of the upper electrode 4, between the carbon from the upper electrode 4 side and the carbon formed on the lower electrode 2. This gap is preferably several nm to several ten nm, and is properly determined according to the time of the step of applying the voltage to the upper electrode and

lower electrode under existence of the organic material detailed hereinafter, the voltage applied, and so on.

The upper electrode is formed on the anodic oxide layer and is preferably made of a metal with excellent electron transmission characteristics, for example, Al.

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Structural examples of the above electronemitting device of the present invention will be explained using the schematic sectional views of Figs. In Figs. 2A to 2D, the same portions as those in Figs. 1A and 1B are denoted by the same reference numerals. There are four kinds of structures illustrated in Figs. 2A to 2D, but other structures may also be employed, without having to be limited to these illustrated structures. The following describes examples using the metal for the upper electrode and the lower electrode, but they may also be made of a semiconductor. The structure of Fig. 2A is metal (lower electrode) 2 / metal oxide layer 3 / pores, each having an electron-emitting body 6 / vacuum / metal (upper electrode) 4. The structure of Fig. 2B is metal (lower electrode) 2 / pores, each having an electronemitting body 6 / vacuum / metal (upper electrode) 4. The structure of Fig. 2C is metal (lower electrode) 2 / metal oxide layer 3 / pores, each having an electronemitting body 6 / vacuum / metal (upper electrode) 4 formed in regions except for regions above the pores.

The structure of Fig. 2D is metal (lower electrode) 2 / pores, each having an electron-emitting body 6 / vacuum / metal (upper electrode) 4 formed in regions except for regions above the pores.

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In the structures of Fig. 2A and Fig. 2C, the metal oxide layer 3 is obtained on the occasion of anodic oxidation of the lower electrode, and two structural regions, a dense film structural region without pores and a film structural region with pores, can be obtained in this metal oxide layer 3, depending upon the anodic oxidation conditions. As illustrated in Fig. 2A and Fig. 2C, the formation of the dense film structural region of the above metal oxide layer between the lower electrode 2 and the electron-emitting bodies 6 in the pores results in forming a nonlinear device in the structure of metal / insulator / electron-emitting bodies (carbon), so as to impart the function of current limitation, which can prevent current fluctuation in discharge or the like on the occasion of driving the electron-emitting device of the present invention and which can in turn prevent damage to the electron-emitting device. A specific production method of the above metal oxide layer will be described hereinafter, but it is first formed, for example, under conditions for forming porous metal oxide and thereafter the thickness of the dense film structural region is adjusted in a widening step of described

hereinafter.

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The structures of Fig. 2B and Fig. 2D do not have the metal oxide layer without the pores and the electron-emitting bodies (carbon) in the pores are electrically connected directly to the lower electrode. These structures are obtained by anodizing the lower electrode, thereafter sufficiently widening the pores by the widening step of pores hereinafter and thereafter the electron-emitting bodies (carbon) are formed in the pores, whereby the electron-emitting bodies are electrically connected to the lower electrode. In another method, the metal oxide layer without the pores between the lower electrode and the metal oxide layer with the pores is electrically broken by pulse voltage applied in the step of forming the electron-emitting bodies (carbon) in the pores of the anodic oxide layer described hereinafter, so that the electron-emitting bodies are electrically connected to the lower electrode. In the structures of Fig. 2B and Fig. 2D, the electron-emitting device is also provided with the nonlinear characteristics by tunneling between the electron-emitting bodies and the vacuum. The above "vacuum" is one equivalent to the vacuum ambience in which the substrate with the electron-emitting device formed thereon is set.

When the upper electrode 4 is present in the portions above the pores as in the structures of Fig.

2A and Fig. 2B, the electron-emitting bodies formed in the pores are in contact with the vacuum through the upper electrode. When the upper electrode 4 is absent in the portions above the pores on the other hand as in the structures of Fig. 2C and Fig. 2D, the electron-emitting bodies formed in the pores are in direct contact with the vacuum.

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With consideration to aspects of heat resistance of the electron-emitting device of the present invention, stability of electron emission characteristics, improvement in repeatability, and so on, the carbon deposit for forming the electron-emitting bodies is preferably at least one of graphite, amorphous carbon and diamondlike carbon.

There are various methods for producing the above-stated electron-emitting device, among which an example is schematically illustrated in a step diagram of Fig. 3. A first production method for producing the structures of Fig. 2C and Fig. 2D will be described below.

The first step is a step of forming the lower electrode of the metal or the semiconductor on the substrate. The substrate 1 is cleaned well with detergent, pure water, and organic solvent or the like, a material for the lower electrode is deposited by vacuum evaporation, sputtering, or the like, and thereafter the lower electrode 2 is formed on the

substrate, for example, by the photolithography technology. The lower electrode may also be formed by plating.

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The second step is a step of anodizing the lower electrode. An anodic oxidation system will be described herein using the conceptual drawing thereof illustrated in Fig. 4. In Fig. 4, numeral 1 represents a substrate, 31 an anodic oxidation tank, 32 an anodic oxidation electrolyte solution, 33 an electrode, 34 a power supply, and 35 an O-ring. The anodic oxidation electrolyte solution 32 for the metal such as Al is an aqueous solution of one selected from inorganic acids such as sulfuric acid, sulfamic acid, and phosphoric acid, and organic acids such as oxalic acid, malonic acid, and succinic acid, and a substance added thereto as solvent is polyhydric alcohol such as ethylene glycol, glycerin, or dextrin. On the other hand, the electrolyte solution for Si is an aqueous solution of Further, an oxidation process such as thermal oxidation may by further added. The electrode 33 is the metal such as Pt. The anodic oxidation of the lower electrode is effected by energization from the power supply 34 with the electrode 33 as a cathode and the substrate 1 as an anode. The geometrical structure of the anodic oxide layer can be controlled by production conditions. Specifically, the spacing between the pores can be controlled by the anodic

oxidation voltage, the depths of the pores by the anodic oxidation time, and the diameters of the pores by such conditions as the composition of the electrolyte solution, the voltage, the current.

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Further, control of the regular pores or the irregular pores can also be made by control of these conditions. Next, the substrate on which the anodic oxide layer was thus formed thereon is dipped in the anodic oxidation electrolyte solution or the like to adjust the diameter of pores and thickness of the dense oxide film (this process will be called widening) and is washed well with water and thereafter dried in vacuum.

The third step is a step of forming the upper electrode on the metal or the semiconductor thus anodized. The upper electrode is formed in the thickness of several nm to several ten nm on the above anodic oxide layer in the same manner as the lower electrode as described above.

The fourth step is a step of forming the electron-emitting bodies in the pores of the anodic oxide layer. This step is a step of forming carbon in the pores of the aforementioned anodic oxide layer by applying the voltage to the upper electrode and lower electrode under existence of the organic material of a gas state. The carbon formed in this step is graphite. The graphite herein is either of so-called HOPG, PG, and GC. HOPG indicates almost perfect graphite crystal

structure, PG somewhat disordered crystal structure having crystal grains of 20 nm or so, and GC more disordered crystal structure having crystal grains of 2 nm or so. In addition, the carbon herein may also be non-crystalline carbon. The non-crystallin_carbon herein includes amorphous carbon and, a mixture of amorphous carbon with fine crystals of graphite.

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Now, a vacuum process system used in the fourth step will be described referring to Fig. 5. In Fig. 5, the same portions as those illustrated in Figs. 1A, 1B and 2A to 2D are denoted by the same reference numerals. In Fig. 5, numeral 55 indicates a vacuum vessel, 56 an exhaust pump, and 57 a supply of organic gas used in formation of carbon in the pores of the anodic oxide layer of the electron-emitting device according to the present invention. The electronemitting device of the present invention is placed in the vacuum vessel 55. Specifically, numeral 1 represents the substrate, 2 the lower electrode, 3 the anodic oxide layer, and 4 the upper electrode. Further, numeral 51 denotes a power supply for applying the device voltage Vf to the electron-emitting device, 50 a current meter for measuring the device current If flowing in the lower electrode 2 and the upper electrode 4, and 54 an anode electrode for capturing the emission current Ie of electrons emitted from the device. Numeral 53 designates a high voltage supply

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for applying the voltage to the anode electrode 54, and 52 a current meter for measuring the emission current Ie emitted from the electron-emitting device. example, supposing the voltage of the anode electrode is in the range of 0 to 10 kV, measurement can be carried out while the distance H between the anode electrode and the electron-emitting device is set in the range of 10 µm to 8 mm. There is provided equipment necessary for the measurement under a vacuum ambience, such as a vacuum gage not illustrated, in the vacuum vessel 55, so as to permit measurement and evaluation under a desired vacuum ambience. exhaust pump 56 is composed of an ordinary high-vacuum system consisting of a turbo pump or a rotary pump and an ultrahigh vacuum system consisting of an ion pump or the like. The whole of the vacuum process system shown herein can be heated up to 350 °C by a heater not illustrated.

The substrate 1 is set in the vacuum vessel and the vacuum vessel is evacuated into a vacuum ambience. Thereafter, the organic gas is introduced from the supply of organic gas 57 into the vacuum vessel 55 and the voltage is applied to the upper electrode and lower electrode under the ambience containing the gas of organic substance. The waveform of the voltage is a waveform of pulses, which are repetitively applied. A method for applying the voltage may be selected from a

method illustrated in Fig. 6A for continuously applying pulses with their pulse peak values of a constant voltage, and a method illustrated in Fig. 6B for applying voltage pulses with increasing pulse peak values.

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In the method of the fixed application direction of the pulse voltage wherein either the upper electrode or the lower electrode is fixed at a higher potential while the other at a lower potential (Fig. 6A), supposing the upper electrode is fixed at the lower potential than the lower electrode, the carbon is formed mainly on the lower electrode side which is kept at the higher potential. In the method for applying the higher potential alternately to the upper electrode and to the lower electrode (Fig. 6B), the carbon is formed both on the upper electrode and on the lower electrode.

In Fig. 6A, T1 and T2 represent the pulse width and the pulse spacing of pulses in the voltage waveform. Normally, T1 is set in the range of 1 microsecond to 10 milliseconds and T2 in the range of 10 microseconds to 100 milliseconds. The peak values of the triangular waves are properly selected according to the form of the electron-emitting device. Under such conditions the voltage is applied, for example, for several minutes to several ten minutes. The pulse waves are not limited only to the triangular waves, but

desired waveforms may be employed including the rectangular waves. Further, T1 and T2 in Fig. 6B can be the same as those illustrated in Fig. 6A. The peak values of the triangular waves can be increased, for example, by steps of about 0.1 V.

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The preferred gas pressure of the organic substance for formation of the carbon differs depending upon the aforementioned application form, the shape of the vacuum vessel, the type of the organic substance, and so on and is thus properly determined according to the circumstances. An appropriate organic substance can be selected from aliphatic hydrocarbons of alkane, alkene, and alkyne, aromatic hydrocarbons, alcohols, aldehydes, ketones, amines, organic acids such as phenol, carboxylic acid, and sulfonic acid, and so on. Specific examples of such substances include saturated hydrocarbons represented by C_nH_{2n+2} such as methane, ethane, and propane, unsaturated hydrocarbons represented by the composition formula of $\boldsymbol{C}_{\boldsymbol{n}}\boldsymbol{H}_{2\boldsymbol{n}}$ or the like such as ethylene and propylene, benzene, toluene, methanol, ethanol, formaldehyde, acetaldehyde, acetone, methyl ethyl ketone, methylamine, ethylamine, phenol, formic acid, acetic acid, propionic acid, and so on. The organic gas is also selected according to the diameter of the pores formed in the anodic oxide layer. This is because adsorption of the organic gas is also dependent on the diameter of the pores.

During this process carbon is deposited from the organic substance present in the ambience into the pores in the anodic oxide layer, whereby the device current If and emission current Ie change remarkably.

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Completion of the fourth step is determined while measuring the device current If and the emission current Ie. The apertures of the upper electrode 4 above the pores, illustrated in Figs. 2C and 2D, are formed in the initial stage of application of the above-stated voltage pulses in this step.

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The fifth step is a stabilization step. Namely, this step is a step of stabilizing the characteristics of the electron-emitting device produced by the first to the fourth steps. The fifth step is a step of removing intermediate products of the organic material and also removing the organic gas, water, oxygen, etc. adsorbing to the substrate etc. from the carbon in the pores of the anodic oxide layer, whereby the step can impart to the device such a property that the device current and the emission current monotonically increase above a certain threshold against the voltage applied to the device. This step is a step of exhausting the organic substance in the vacuum vessel and an evacuation apparatus for evacuating the vacuum vessel is preferably one not using oil in order to avoid influence of the oil from the apparatus on the characteristics of the device.

Specifically, the evacuation apparatus can be selected from a sorption pump, an ion pump, and so on.

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The partial pressure of the organic component in the evacuation apparatus is set to a partial pressure under which there is little carbon or carbon compound newly deposited, and is preferably not more than 1×10^{-8} Torr and particularly preferably not more than 1×10^{-10} Torr. It is further preferred that the whole of the vacuum apparatus be heated during evacuation of the inside of the vacuum apparatus so as to facilitate removal of molecules of the organic substance adsorbing to the inner wall of the vacuum apparatus and to the electron-emitting device. The heating condition at this time is desirably the temperature of 150 to 300 °C and the heating time of not less than several hours, but the heating condition is not limited particularly to this condition.

The ambience during driving after completion of the stabilization step is preferably maintained in the ambience at the end of the above stabilization operation, but it is not limited to this. Sufficient characteristics can be maintained by an ambience from which the organic substance is removed adequately but the vacuum degree of which is a little degraded. By employing such a vacuum ambience, deposition of new carbon substance can be suppressed, whereby the device current If and emission current Ie are stabilized as a

result.

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Next, a second production method, which is a method for forming carbon or diamondlike carbon in a liquid, will be described referring to the step diagram of Fig. 3. The following describes an example for producing the structures of Fig. 2A and Fig. 2B.

The first step is a step of forming the lower electrode of the metal or the semiconductor on the substrate, which is carried out in the same manner as the method described in the first step of the first production method.

The second step is a step of anodizing the lower electrode, which is similar to the method described in the second step of the first production step, but in which after the anodic oxidation, the substrate with the anodic oxide layer formed thereon is washed with water, dipped in the anodic electrolyte solution (that is "widening") and then is taken into the electrolytic tank of step 3.

The third step is a step of forming the electron-emitting bodies in the pores of the anodic oxide layer under existence of a liquid organic material. This step is a step of forming the electron-emitting bodies in the pores of the aforementioned anodic oxide layer by applying the voltage to the electrode 33 and the lower electrode of Fig. 4. Using the same apparatus as illustrated in Fig. 4.

electrolysis is effected in an electrolyte solution of alcohol with the lower electrode as an anode and with the electrode 33 of Fig. 4 as a cathode, whereby diamondlike carbon can be deposited into the pores formed by the anodic oxidation from the lower electrode side. The diamondlike carbon grows in a columnar shape in the pores with a lapse of the electrolytic time.

The fourth step is a step of forming the upper electrode on the metal or the semiconductor thus anodized, in which the upper electrode is formed in the thickness of several nm to several ten nm over the above anodic oxide layer in the same manner as the aforementioned lower electrode was.

The fifth step is a stabilization step, which is carried out in the same manner as the stabilization step described in the fifth step of the first production method.

[Example 1 of the first embodiment]

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Fig. 7A is a plan view of a substrate on which five electron-emitting devices of the present invention are placed and Fig. 7B is a schematic sectional view along 7B-7B of Fig. 7A.

In Figs. 7A and 7B, numeral 1 denotes a substrate, 73 anodic oxide layers, 71 lead wires of the lower electrodes, 72 a lead wire of the upper electrodes, and 74 intersections between the lead wires 71 of the lower electrodes and the lead wire 72 of the

upper electrodes, at which the electron-emitting devices of the present invention are placed.

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In the present example, substrates, each including five electron-emitting devices in either one of the structures of the four types illustrated in Figs. 2A, 2B, 2C, and 2D, will be called substrates A, B, C, and D, respectively.

A production method of the present example will be described specifically.

10 (Step 1: step of forming the lower electrode of metal on the substrate)

with detergent, pure water, and organic solvent or the like, the material of Al for the lower electrode was deposited in the thickness of 200 nm by sputtering, and thereafter the lower electrode wires 71 were formed in a stripe pattern on the substrate 1 by the photolithography technology. The lower electrode wires 71 were covered in part by a known mask resin for plating in order to use parts of the lower lead wires 71 as terminals.

(Step 2: step of anodizing the lower electrodes)

Using the anodic oxidation system illustrated in Fig. 4, the lower electrodes of Al prepared in step 1 were anodized. For the substrates B and D, an aqueous solution of oxalic acid 30 g/l was used as an anodic oxidation electrolyte solution (32 in Fig. 4).

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A Pt electrode was used as the electrode (33 in Fig. The anodic oxidation was carried out at the constant voltage of 45 V from the power supply (34 in Fig. 4) with the electrode (33 in Fig. 4) as a cathode and the lower wires (71 in Figs. 7A and 7B) provided on the substrate 1, as anodes. On this occasion, the initial current density was 400 mA/cm2, but it decreased with progress of anodic oxidation. Next, the substrate with the anodic oxide layers formed thereon was dipped in H₃PO₄ solution, washed well with water and thereafter dried in vacuum. The above anodic oxidation step resulted in forming the pores in the anodic oxide layers. For the substrates A and C, the anodic oxide layers with pores were formed under the same anodic oxidation conditions as in the case of the substrates B and D. A thickness of dense film is controlled by dipping in phosphoric acid solution in a shorter time than that of the cases of the substrates B and D. (Step 3: step of forming the upper electrode on the metal or the semiconductor thus anodized)

The upper electrode 72 was formed in the thickness of 10 nm on the above anodic oxide layers of each of the substrates A, B, C, and D in the same manner as the above lower electrodes had been formed. (Step 4: step of forming carbon in the pores of the anodic oxide layers (under existence of a gas organic material))

The substrate 1 was placed in the vacuum chamber also serving as a measuring device and the voltage was applied to the upper electrode and lower electrode under an ambience containing gas of acetone at 10⁻¹ Pa. The voltage was applied for thirty minutes in the form of rectangular waves having the pulse width T1 of 1 ms and the pulse spacing T2 of 10 ms in the pulse waveform of Fig. 6A. At the same time, the current of device was monitored. The voltage was 10 V in the substrate A, B, C, or D. Apertures are formed in the upper electrode above the pores by the application of the above-stated voltage pulses in this step. (Step 5: stabilization step)

Next, the acetone gas was exhausted well and thereafter the system was evacuated for ten hours while being heated at 250 °C.

(Step 6: step of again forming the upper electrode)

For the substrates A and B, the upper electrode was again formed in the same manner as above, thereby forming the structures of Figs. 2A and 2B.

[Comparative Example]

(Step 1) to (step 4) were carried out under the production conditions of substrate B, thereby separately preparing a substrate without execution of (step 5: stabilization step). This will be called substrate E.

[Results]

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Then the substrate A, B, C, D, or E was set in the vacuum process system of Fig. 5, the voltage was applied to the lower electrode and upper electrode of each device, and to the anode electrode under an ultrahigh vacuum, and the currents (the device current and emission current) and device voltage characteristics were measured. Figs. 8A and 8B show the current/voltage characteristics. At the same time, it was checked whether the voltage-controlled negative resistance (VCNR characteristics) occurred with slowly sweeping the device voltage. Further, emission of electron beam was observed by emission of a fluorescent member placed at the anode. After the measurements, the samples thus formed were then observed with an electron microscope, plane TEM, and so on.

As apparent from the current/voltage characteristics of Figs. 8A and 8B, the device current and emission current of the substrates A, B, C, and D demonstrate monotonically increasing characteristics above their threshold. The current was negligible below the threshold (which will be called Vth). These verify that the devices are nonlinear devices demonstrating the nonlinear characteristics of the device current and emission current. On the other hand, it is seen that the substrate E of the comparative example demonstrates the emission current of characteristics that are not the voltage-controlled

negative resistance characteristics (VCNR characteristics), but the device current of the voltage-controlled negative resistance characteristics (VCNR characteristics).

Since the substrates A and C have the structure of the dense anodic oxide layer / the anodic oxide layer having the pores, formed on the lower electrode, it is seen that this structure shifts Vth to the higher device voltage than that of the substrates B and D.

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The diameter of the electron beam observed at the anode electrode was nearly equal to the overlapping part of the upper electrode with the lower electrode.

When the devices were observed with the electron microscope, the regular pores as illustrated in Fig. 1B were observed in the anodic oxide layer in either of the substrates. The diameter of the pores was 200 nm and the density of the pores was 3×10^8 pores/cm².

The upper electrode exists above the pores in the substrates A and B, whereas the upper electrode does not exist above the pores but does exist around the pores in the substrates C and D. This is because the upper electrode above the pores was removed in the case of the substrates C and D on the occasion of applying the pulse voltage in the step of forming the electron-emitting bodies.

Further, plane TEM samples were prepared and

observed, and it was verified that graphite-nature carbon existed in the pores in either sample. It seemed that more carbon was deposited in the pores in the substrate E. The deposit further contained carbon other than graphite.

The present example substantiated the following. First, graphite-nature carbon can be formed in the pores of the anodized layer obtained by anodic oxidation of metal. Second, the devices obtained can function as electron-emitting devices. Third, the stabilization step does not cause the voltagecontrolled negative resistance characteristics (VCNR characteristics) and both the device current and emission current exhibit the monotonic increase characteristics. Fourth, where the anodic oxide layer is the one having the dense anodic oxide layer functioning as an insulating layer and the anodic oxide layer having the pores, the current/voltage characteristics are shifted to the higher voltage side of the device voltage. Fifth, the diameter of the electron beam observed at the anode electrode is nearly equal to the overlapping part of the upper electrode with the lower electrode and there is thus a little divergence of the beam.

25 [Example 2 of the first embodiment]

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The present example is an example in which diamondlike carbon is formed in the pores of the

insulating layer, in liquid. A production method of the present example will be described specifically, again referring to Fig. 3.

(Step 1: step of forming the lower electrode)

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A P-type Si wafer was used as a substrate.

Here, the P-type wafer substrate functions as a lower electrode.

(Step 2: step of anodizing the lower electrode)

Using the apparatus of Fig. 4, the anodic

oxidation operation was carried out in the aqueous solution of HF with the P-type Si wafer as an anode and Pt as a cathode (33 in Fig. 4), and thereafter the wafer was washed with water and then taken into the electrolytic tank of step 3.

15 (Step 3: step of forming the electron-emitting bodies in the pores of the anodic oxide layer (under existence of liquid organic material))

This step is a step of forming carbon in the pores of the anodic oxide layer by applying the voltage under existence of an organic material of a liquid state. Using the system similar to that of Fig. 4, electrolysis was carried out in the electrolyte solution of ethyl alcohol for one hour by applying the voltage between the anode of the lower electrode side of device and the cathode Pt (the electrode 33 of Fig. 4). During the electrolysis the temperature of the solution was controlled at 60 °C by heating the

solution with an unrepresented heater. Then the substrate with the anodic oxide layer was washed well with water and thereafter dried in vacuum.

(Step 4: step of forming the upper electrode)

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A Pt film was deposited as an upper electrode in the thickness of 10 nm by sputtering.

(Step 5: stabilization step)

The stabilization step was carried out in the same manner as in Example 1 above.

10 In the last stage, the above sample was set in the vacuum process system of Fig. 5, and the voltage was applied to the lower electrode and the upper electrode, and to the anode electrode to measure the currents (device currents and emission current) and the 15 device voltage characteristics in the same manner as in Example 1. At the same time, it was checked whether the voltage-controlled negative resistance characteristics (VCNR characteristics) appeared with slowly sweeping the device voltage. After the 20 measurements, the sample thus formed was observed with the electron microscope, the plane TEM, and so on.

The current/voltage characteristics of both the device current and emission current were the monotonically increasing characteristics over their threshold and the current was negligible below the threshold, as in Example 1. These verified that the device was a nonlinear device demonstrating the

nonlinear characteristics of both the device current and emission current. The emission current was five times greater than those of the devices of Example 1. This is conceivably because of decrease of work function of carbon in the pores or influence of shape.

In observation with the electron microscope, the holes of the porous structure were observed.

Further, Raman and plane TEM samples were prepared and observed, and it was proved thereby that diamondlike carbon existed in the holes.

[Example 3 of the first embodiment]

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The present example is an example of application to an image pickup device in which a plurality of electron-emitting devices, which were prepared by a method similar to that in Example 1, are placed in a two-dimensional array on a substrate. Fig. 9A and Fig. 9B are schematic views of the image pickup device of the present invention. Fig. 9A is a sectional view of an image pickup tube of the present invention and Fig. 9B is a plan view of the substrate on which the electron-emitting devices are placed. Figs. 9A and 9B, numeral 91 designates an electronemitting device substrate (an electron source substrate), 92 lower electrodes (wires), 93 anodic oxide layers, 94 upper electrodes (wires), 95 a photoconductive member, 96 a transparent electrode, 97 a photoconductive member substrate, 98 a device voltage applying source, and 99 a power supply for applying the voltage to the photoconductive member. In Fig. 9A, the electron-emitting device substrate and the photoconductive member substrate are bonded to a support frame not illustrated, thereby composing a hermetically closed container. The inside of the container is maintained in a high vacuum. Although Fig. 9A is illustrated so that one of the upper electrodes is connected to the device voltage applying source, it is noted that all the upper electrodes are connected to the device voltage applying source.

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Next described is the principle of the image pickup device of the present example. The operation of the image pickup device of the present example is similar to that of the conventional image pickup tubes, but the image pickup device of the present example is different from the conventional image pickup tubes in that an image is read using electron beams from the electron-emitting devices arrayed in the twodimensional pattern and in that the image pickup device does not have a converging system for converging the electron beams. When light is incident to the photoconductive member 95, holes are created in the photoconductive member 95 by the incident light. holes are accelerated toward the electron-emitting device substrate 91 by an electric field applied to the photoconductive member 95, so as to undergo avalanche

multiplication. On the other hand, electron beams emerge from the electron-emitting device substrate 91. Electrons are injected into the photoconductive member 95 in the number corresponding to the holes accumulated therein, and excessive electron beams return to the electron-emitting device substrate 91 to flow in the upper wires 94. In this way, signal current according to the holes generated in response to the incident light is outputted from a signal current amplifier.

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Next, the structure of the image pickup device of the present example will be described. Over the electron-emitting device substrate 91, the anodic oxide layers 93 are formed in regions except for the lead portions of wires on the lower electrode wires 92, and the upper wires 94 are formed perpendicularly to the lower electrode wires 92. Intersecting portions between the lower electrode wires 92 and the upper wires 94 constitute the electron-emitting regions similar to those in Figs. 1A and 1B. The size of the electron-emitting device is 50 µm square. The photoconductive member 95 is made of Se and the thickness thereof is 4 µm. The separation between the electron-emitting device substrate 91 and the photoconductive member substrate 97 is 1 mm.

A method for producing the image pickup device of the present example will be described below. The side of electron-emitting device substrate 91 was

prepared in the same manner as in the example.

Further, the photoconductive member 95 was deposited by a resistance heating evaporation method of Se. The electron-emitting device substrate and the photoconductive member substrate thus prepared were bonded to the unrepresented support frame. After the inside was evacuated through an exhaust pipe not illustrated, a hermetically closed container was formed. Then the image pickup device thus produced was operated based on the principle of operation described previously and the signal current was obtained in 1:1 correspondence to the size of the electron-emitting devices. The operation was thus confirmed.

[Example 4 of the first embodiment]

The present example is an example of construction of a display device in which a plurality of electron-emitting devices, which were prepared in a method similar to that in Example 2, are placed in a two-dimensional array on a substrate. Figs. 10A and 10B are schematic views of the display device of the present invention. Fig. 10A is a schematic sectional view of the display device of the present invention and Fig. 10B is a plan view of the substrate on which the electron-emitting devices are placed. In Figs. 10A and 10B, numeral 100 represents a rear plate, 101 an electron-emitting device substrate (an electron source substrate), 102 lower electrodes (wires), 103 anodic

oxide layers, 104 upper electrodes (wires), 105 a metal back, 106 a fluorescent member, 107 a face plate, 108 a device voltage applying source, and 109 a high voltage supply for the anode. In Fig. 10A, the electronemitting device substrate and the face plate are bonded to an unrepresented support frame to compose a hermetically closed container and the inside thereof is maintained in a high vacuum. Although Fig. 10A is illustrated so that one of the upper electrodes is connected to the device voltage applying source, it is noted that all the upper electrodes are connected to the device voltage applying source. The fluorescent member 106 is formed in a stripe pattern in which black stripes divide fluorescent materials of R (red), G (green), and B (blue) not illustrated, from each other.

Next described is the principle of the display device of the present example. In the display device of the present example, each electron-emitting device line in the two-dimensional array is selected by a scanning signal from the outside and electron beams are emitted from the devices in the electron-emitting device line selected with being modulated by a modulation signal from the outside. The electron beams emitted diverge a little in the electron-emitting devices of the present invention. Thus, the electron beams are accelerated without using a converging system of electron beam and are incident to the metal back/the

fluorescent member to cause luminescence. An image is displayed in this way.

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The structure of the display device of the present example will be described below. Over the electron-emitting device substrate 101 the anodic oxide layers 103 are formed in regions except for the lead portions of wires on the lower electrode wires 102, and the upper wires 104 are formed perpendicularly to the lower electrode wires 102. Intersecting portions between the lower electrode wires 102 and the upper wires 104 constitute the electron-emitting devices similar to that in Figs. 1A and 1B. The display device was composed of $200 \times (160 \times 3 \text{ (i.e., R, G, and B)})$ electron-emitting devices. Figs. 10A and 10B show those in part. The size of the electron-emitting device is 40 µm square. The fluorescent member 106 was high-acceleration fluorescent material P22 for CRT. The separation between the electron-emitting device substrate 101 and the face plate 107 was 2 mm. voltage of 5 kV was applied to the metal back 105.

A method for producing the display device of the present example will be described below. (Step 1: step of forming the lower electrodes of the metal or the semiconductor on the substrate 101)

The substrate was an n-type Si wafer. A plurality of stripes of P-type portions were formed in the n-type Si wafer. The stripes of the P-type

portions function as the lower electrodes.

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(Step 2: step of anodizing the lower electrodes)

Using the apparatus of Fig. 4, the anodic oxidation operation was carried out in the aqueous solution of HF with the P-type portions of the Si wafer as anodes and Pt as a cathode, and thereafter the wafer was washed with water and then taken into the electrolytic tank of step 3. The anodic oxide layers were selectively formed in the stripes of the P-type portions.

(Step 3: step of forming the electron-emitting bodies in the pores of the anodic oxide layers (under existence of organic material of liquid state))

This step is a step of forming the electron-15 emitting bodies in the pores of the anodic oxide layers by applying the voltage to the upper electrodes and lower electrodes under existence of an organic material of a liquid state. Using the apparatus similar to that of Fig. 4, electrolysis was brought about in the 20 electrolyte solution of ethyl alcohol for one hour between the cathode of the lower electrode side and the During the electrolysis the temperature of the solution was controlled at 60 °C by heating the solution by the heater not illustrated. Then the 25 substrate with the anodic oxide layers was washed well with water and thereafter dried in vacuum. (Step 4: step of forming the upper electrodes on the

metal or semiconductor thus anodized)

The upper electrodes were formed in the thickness of 10 nm by sputtering of Pt. (Step 5: stabilization step)

The stabilization step was carried out in the same manner as in above Example 1.

The fluorescent materials of R, G, and B were formed in stripes on the face plate 107 and after filming thereof, the metal back 105 was deposited by evaporation. The electron-emitting device substrate 101 prepared as described above was placed on the rear plate 100 and the face plate 107 was bonded to the unrepresented support frame. After the inside was evacuated through an exhaust pipe not illustrated, a hermetically closed container was constructed.

Then the display device thus produced was operated based on the principle of operation described previously and it was verified that a bright image was displayed in high definition.

20 [Second Embodiment]

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Fig. 11A is a sectional view of the second embodiment. Fig. 11B is a partly enlarged, schematic view of part A in the sectional view of Fig. 11A. The present embodiment uses the anodic oxide layer for the insulating layer. In Fig. 11A reference numerals are given in the similar fashion to those in Figs. 1A and 1B.

The substrate 1 to be employed herein can be selected from quartz glass, glass with a decreased content of impurity such as Na, soda lime glass, a glass substrate obtained by depositing SiO₂ on soda lime glass by sputtering or the like, ceramics such as alumina, an Si substrate, an Si substrate with a deposited layer of SiO₂, and so on. Particularly, when the substrate 1 is a semiconductor substrate, a driver or the like for driving the electron-emitting device can also be mounted simultaneously.

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The lower electrode 2 is selected from metals, such as Al, Ta, Nb, Ti, Zr, Hf, or Si, and semiconductors that can undergo anodic oxidation. The thickness of the lower electrode 2 is properly determined according to the thickness of the anodic oxide layer, the electrical resistance of the lower electrode, and so on. The materials for the lower electrode are not limited to only the metals that can be anodized, but they may also be of a stack form of a metal that cannot be anodized and a metal that can be anodized.

The anodic oxide layer 3 is formed by anodic oxidation of the lower electrode in part. In the anodic oxide layer 3 there exist regular or irregular pores 5. This will also be called porous structure in the present specification. The regular or irregular pores 5 can be formed by selecting anodic oxidation

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conditions including a composition of an anodic oxidation bath, the temperature of the bath, the voltage, the time, etc., according to the material for the lower electrode 2. Preferably, the regular pores are selected. Diameters of the pores range from several ten nm to several hundred nm and depths thereof from several ten nm to several thousand nm. density of the pores is 10^8 to 10^{12} pores/cm². The shape of the pores is not limited only to the circle, but the ellipse, square, etc. can also be applied to the electron-emitting devices of the present invention. The variety of shapes can also be formed using the focused ion beam or the like. Therefore, the expression "length of pore" will also be used in place of the diameter of pore in the present invention. each pore 5, carbon 6 electrically connected to the lower electrode 2 is formed in a rim shape along the inner wall of pore. Electrons are emitted from the rim-shape part on the inner wall in each pore, thus achieving linear electron emission from each pore according to the shape of the pore.

The carbon may also be formed in the similar fashion from the side of the upper electrode 4.

There is a gap created between the carbon formed on the lower electrode 2, and the upper electrode or, in the case where the carbon is also formed from the side of the upper electrode 4, between

the carbon from the upper electrode 4 side and the carbon formed on the lower electrode 2. This gap is preferably several nm to several ten nm, and is properly determined according to the time of the step of applying the voltage to the upper electrode and lower electrode under existence of the organic material detailed hereinafter, the voltage applied, and so on.

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The upper electrode is formed above the anodic oxide layer and is made preferably of a material having a high melting point, such as Pt, W, Mo, or Hf.

Structural examples of the above electronemitting device of the present invention will be explained using the schematic sectional views of Figs. 12A to 12D. In Figs. 12A to 12D, the same portions as those in Figs. 11A and 11B are denoted by the same reference numerals. In the figures reference numeral 7 designates an electroconductive member of metal or the like and 8 a small gap between the upper electrode and the electron-emitting bodies. There are four kinds of structures illustrated in Figs. 12A to 12D, but other structures may also be employed, without having to be limited to these illustrated structures. The following describes examples using the metal for the upper electrode and the lower electrode, but they may also be made of the semiconductor.

The structure of Fig. 12A is metal (lower electrode) / metal oxide layer / pores, each having a

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rim-shape electron-emitting body 6 along the inner wall of pore / vacuum / metal (upper electrode) 4 formed in the regions except for the regions above the pores. The structure of Fig. 12B is metal (lower electrode) / pores, each having a rim-shape electron-emitting body 6 along the inner wall of pore / vacuum / metal (upper electrode) 4 formed in the regions except for the regions above the pores. The structure of Fig. 12C is metal (lower electrode) / metal oxide layer / pores, each having a pole-shaped electroconductive member 7 and a rim-shape electron-emitting body 6 along the inner wall of pore / vacuum / metal (upper electrode) 4 formed in the regions except for the regions above the The structure of Fig. 12D is metal (lower electrode) / pores, each having a pole-shaped electroconductive member 7 and a rim-shape electronemitting body 6 along the inner wall of pore / vacuum / metal (upper electrode) 4 formed in the regions except for the regions above the pores.

In the structures of Fig. 12A and Fig. 12C, the metal oxide layer 3 is obtained on the occasion of anodic oxidation of the lower electrode, and two structural regions, a dense film structural region without pores and a film structural region with pores, can be obtained in this metal oxide layer 3, depending upon the anodic oxidation conditions. As illustrated in Fig. 12A and Fig. 12C, the formation of the dense

film structural region of the above metal oxide layer between the lower electrode 2 and the electron-emitting bodies 6 in the pores results in forming a nonlinear device in the structure of metal / insulator / rimshape electron-emitting bodies, so as to impart the function of current limitation, which can prevent current fluctuation in discharge or the like on the occasion of driving the electron-emitting device of the present invention and which can in turn prevent damage to the electron-emitting device. A specific production method of the above metal oxide layer will be described hereinafter, but it is first formed, for example, under conditions for forming the porous metal oxide and thereafter the thickness of the dense film structural region is adjusted in a widening step of pores described hereinafter.

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The structures of Fig. 12B and Fig. 12D do not have the metal oxide layer without the pores and the electron-emitting bodies (carbon) in the pores are electrically connected directly to the lower electrode. This structure is constructed by anodizing the lower electrode, thereafter sufficiently widening the pores by the widening step of pores described hereinafter, and further forming the electron-emitting bodies (carbon) in the pores, whereby the lower electrode becomes electrically connected to the electron-emitting bodies. On this occasion, the metal oxide layer

without the pores between the lower electrode and the metal oxide layer with the pores may be electrically broken by the pulse voltage applied in the step of forming the carbon in the pores of the anodic oxide layer described hereinafter, so that the electronemitting bodies are electrically connected to the lower electrode in some cases.

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In the structures of Fig. 12B and Fig. 12D, the electron-emitting device is also provided with the nonlinear characteristics by tunneling between the electron-emitting bodies and the vacuum. In the structures of Fig. 12C and Fig. 12D, there are the pole-shaped electroconductive bodies and the rim-shaped electron-emitting bodies along the inner walls of pores, in the pores. In these cases, the conductive bodies decrease the resistance of the region from the lower electrode to the electron-emitting bodies, so that the insulating layer can be formed in larger thickness, so as to decrease the capacitance between the lower electrode and the upper electrode, which is advantageous in terms of driving.

The electrical connection with the lower electrode can also be achieved in such a way that the metal is precipitated by alternating current into the pores of the anodic oxide film by the coloring method of the anodic oxide film conventionally well known whereupon the precipitating metal into the pores

migrates into the dense anodic oxide film to implement the electrical connection. The above "vacuum" is one equivalent to the vacuum ambience in which the substrate with the electron-emitting device formed thereon is set.

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In the electron-emitting device of the present invention described above, the carbon making the electron-emitting bodies is preferably at least one of graphite, amorphous carbon, and diamondlike carbon, particularly, in terms of heat resistance, stability of electron emission characteristics, and improvement in repeatability, as stated previously.

Next described is an electron-emitting mechanism of the electron-emitting device of the present invention in the structural examples of Figs. 12A to 12D. In the surface conduction electronemitting device stated previously in the related background art, according to Japanese Laid-open Patent Application No. 9-82214, electrons are once emitted into the vacuum outside the anode from a certain position on the anode side (which is also called the higher potential side) of the fissure region, in the fissure region of the surface conduction electronemitting device. The electrons once emitted move in the electric field created by the cathode (which is also called the lower potential side) and the anode, and electrons flying over the singular point

(hereinafter referred to as a stagnation point) of the electric field are attracted to the anode plate by the electric field created by the voltage applied thereto. The electrons that do not reach the singular point of the electric field drop onto the anode, and some of electrons are scattered here to be deflected and again emitted into the vacuum. Electrons moving over the singular point of the electric field as a result of repetition of this scattering also reach the anode plate.

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It is described in the prior art application that, in order to largely increase the electron emission efficiency, the electric field needs to be set in such conditions that most of the electrons once emitted are attracted to the anode plate without dropping onto the anode in the above mechanism of electron emission and that the electron emission efficiency can be increased by providing the field correcting electrode outside the device electrode and applying a sufficiently higher voltage thereto than the voltage applied to the device for emission of electron.

In contrast with it, in the case of the electron-emitting device of the present invention, when the higher potential is applied to the upper electrode and the lower potential than that to the upper electrode is applied to the lower electrode, a potential difference between them is placed in the

small gap between the upper electrode 4 and the electron-emitting bodies 6, whereupon electrons are emitted from the electron-emitting bodies into the vacuum. Since a strong electric field is placed in the small gap corresponding to the fissure of the aforementioned prior art, the electrons emitted from the electron-emitting bodies 6 into the vacuum collide with the upper electrode 4 to be scattered, just as in the case of the surface conduction electron-emitting device described previously in the related background art. It is, however, assumed that, in the case of the electron-emitting device of the present invention, the electrons reach the anode plate over the singular point of the electric field without repetition of scattering.

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Fig. 13 is a diagram to show the principle of the electron-emitting device of the present invention. Fig. 13 is a schematic sectional view of Fig. 12D. In Fig. 13 the portions denoted by the same reference numerals as those in Fig. 12D indicate the same portions. In the figure, h indicates the distance between the electron-emitting device and the anode plate, d the length of pore, and Va the potential of the anode plate.

The following discussion is made with focusing attention on electrons emitted from the electron-emitting body 6 on one side. The electrons emitted from the electron-emitting body 6 into the vacuum

collide with the upper electrode 4 because of the electric field placed in the small gap to be first scattered isotropically. Since the strong electric field from the upper electrode 34 present at the very close distance considerably decreases the stagnation point described above, as compared with that in the conventional surface conduction electron-emitting device, the electrons isotropically scattered reach the anode plate without repetitive scattering, mostly after scattered only once. On the other hand, where the thickness of the upper electrode 4 is small, the electrons also reach the anode plate, mostly after scattered only once, without repetitive scattering. It is considered that the above accounts for the increase of the electron emission efficiency.

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An important factor for the effect of the electric field of the upper electrode opposite to the upper electrode 4 is the diameter of the aperture. Supposing the work function of the conductive electron-emitting body is 4 to 5.5 eV, the electric field for emission of electrons into the small gap is not less than 10⁷ V/cm. When the stagnation point being the singular point of the electric field as defined in the aforementioned prior art is applied to the prior art electron-emitting device and the present invention, the distance Xs of the stagnation point without 34 is represented by the following equation.

 $Xs = h \cdot Vf/(\pi \cdot Va)$

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On the other hand, the stagnation point Xs' with 34 is indicated by the following equation.

 $Xs' = h \cdot Vf / \{\pi \cdot Va + h \cdot Vf / (\pi \cdot d)\}$

Therefore, the smaller the diameter of the aperture, the more the stagnation point is constricted.

Particularly, from the reason that the constriction effect of the stagnation point can be expected even at the upper electrode voltage of several ten V, the diameter of the aperture is preferably not more than 0.5 µm and more preferably not more than 0.2 µm.

Further, since the conductive electron-emitting body is present along the inner wall of pore, the wall in the pore is kept at one potential, which further constricts the aforementioned stagnation point. This further increases the electron emission efficiency.

The effect of the formation of the rim-shape electron-emitting body on the electron emission efficiency can be expected before the depth of the pore indicating the same potential becomes nearly equal to the diameter of the pore.

Further, the thickness of the upper electrode is preferably as thin as possible in order to suppress the repetitive scattering and, from examples, the thickness is preferably not more than 0.2 μ m in terms of the efficiency. For specifying the condition by the thickness of the upper electrode, the small gap

contributing to the emission of electrons has to be present at the edge of the upper electrode. From the viewpoint of suppressing the repetitive scattering, it corresponds to the distance from the small gap to the upper surface of the upper electrode.

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The driving voltage is a low driving voltage, because the gap is small. Since the direction of the voltage to draw the electrons is coincident with the direction toward the anode plate, a spread of the electron beam, though scattered isotropically, is suppressed relatively.

There are a variety of methods for producing the electron-emitting device described above, among which an example will be described referring to the step diagram of Fig. 14.

(Step 1) Step of forming the lower electrode of the metal or the semiconductor on the substrate

The substrate 1 is cleaned well with detergent, pure water, and organic solvent or the like, the material for the lower electrode is deposited by vacuum evaporation, sputtering, or the like, and thereafter the lower electrode 2 is formed on the substrate, for example, by the photolithography technology. The lower electrode may also be formed by electrolytic crystallization.

(Step 2) Step of anodizing the lower electrode
An anodic oxidation system will be first

described herein using the conceptual drawing thereof illustrated in Fig. 15. Numeral 51 denotes an anodic oxidation tank, 52 an anodic oxidation electrolyte solution, 53 an electrode, 54 an anodic oxidation power supply, 55 a temperature controller for controlling the temperature of the anodic oxidation electrolyte solution 52, 56 a vessel for water circulating in the temperature controller, and 57 the circulating water for control of temperature.

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The anodic oxidation electrolyte solution 52 for the metal such as Al is an aqueous solution of one selected from inorganic acids such as sulfuric acid, sulfamic acid, and phosphoric acid, and organic acids such as oxalic acid, malonic acid, and succinic acid, and the substance added thereto as solvent is polyhydric alcohol such as ethylene glycol, glycerin, or dextrin. On the other hand, the electrolyte solution for Si is an aqueous solution of HF. Further, an oxidation process such as thermal oxidation may be further added.

The electrode 53 is the metal such as Pt. The anodic oxidation of the lower electrode is effected by energization from the power supply 54 with the electrode 53 as a cathode and the substrate 1 with the lower electrode formed thereon, as an anode. The geometrical structure of the anodic oxide layer can be controlled by production conditions. Specifically, the

spacing between the pores can be controlled by the anodic oxidation voltage, the depths of the pores by the anodic oxidation time, and the diameters of the pores by such conditions as the composition of the electrolyte solution, the voltage, the current.

Further, control of the regular pores or the irregular pores can also be made by control of these conditions.

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Next, the substrate with the anodic oxide layer formed thereon is dipped in the anodic oxidation electrolyte solution or the like to adjust the diameter of the pores and the thickness of the dense oxide film. (This step will be called widening.) Then the substrate is washed well with water and then dried in vacuum.

(Step 3) Step of forming the upper electrode on the metal or the semiconductor thus anodized

The upper electrode is formed in the thickness of not more than 200 nm in the same manner as the lower electrode was.

(Step 4) Step of forming the electron-emitting bodies in the pores of the anodic oxide layer (under existence of organic material of gas state)

This step is a step of forming carbon in the pores of the aforementioned anodic oxide layer by applying the voltage to the upper electrode and lower electrode under existence of the organic material of a gas state. The carbon formed in this step is, for

example, graphite (including so-called HOPG, PG, and GC). HOPG indicates the almost perfect graphite crystal structure, PG somewhat disordered crystal structure having crystal grains of 20 nm or so, and GC more disordered crystal structure having the crystal grains of 2 nm or so. In addition, the carbon herein may also be non-crystalline carbon (which means amorphous carbon and, a mixture of amorphous carbon with fine crystals of the aforementioned graphite).

10 [Example 1 of the second embodiment]

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The electron-emitting devices were produced in the same structure as in Figs. 7A and 7B.

Production steps of the present example will be described specifically referring to Fig. 14.

15 (Step 1: step of forming the lower electrodes of metal on substrate)

The substrate 1 was prepared by depositing SiO_2 in the thickness of 1 µm on soda lime glass and the substrate 1 was washed well with detergent, pure water, and organic solvent or the like. Then the material of Al for the lower electrodes was deposited in the thickness of 500 nm on the substrate by sputtering and thereafter the lower electrode wires 71 were formed in stripes on the substrate 1 by the photolithography technology. For using parts of the lower lead wires 71 as terminals, they were covered with a known mask resin for plating.

(Step 2: step of anodizing the lower electrodes)

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Using the apparatus of Fig. 15, the anodic oxidation was carried out to anodize parts of the Al lower electrodes prepared in (step 1). The anodic oxidation electrolyte solution 52 was an aqueous solution of oxalic acid 30 q/l. The electrode 53 was the Pt electrode. The anodic oxidation was carried on at 5 °C for five minutes by the constant voltage of 40 V from the power supply 55 with the cathode of the electrode 53 and the anode of the lower wires 71 provided on the substrate 1. On this occasion, the initial current density was 300 mA/cm2, but the current density decreased with progress of the anodic oxidation and thereafter increased once to be saturated. the substrate with the anodic oxide layers was immersed in an aqueous solution of phosphoric acid for thirty minutes to remove the dense anodic oxide layer and thereafter washed well with water.

(Step 3: step of forming columnar metal in the pores of the anodic oxide layers)

Formation of the columnar metal in the pores was carried out using the system of Fig. 16.

In Fig. 16, portions with the same reference numerals as those in Fig. 15 indicate like portions.

Numeral 91 represents a counter electrode for electrolytic deposition of metal, which is a counter electrode made of an inactive electrode such as carbon

or Pt or the same material as the electrodeposited metal. Numeral 92 indicates a container for a metal electrodeposition liquid, 93 a power supply for electrodeposition, and 94 an electrodeposition solution containing the metal.

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In this step Ni was electrodeposited by the constant current at the current density of 1 mA/cm², using the Pt electrode as the counter electrode 91 and 5 % NiSO4 and 4 % H3BO3 as the electrodeposition solution 94 containing the metal. An electrodeposition amount of columnar Ni was controlled by time and the columnar Ni was formed in each pore. The electrodeposition time was 100 seconds.

(Step 4: step of forming the upper electrode on the metal or the semiconductor thus anodized)

The upper electrode 82 was formed in the thickness of 10 nm in the same manner as the lower electrodes were.

(Step 5: step of forming carbon in the pores of the anodic oxide layers (under existence of organic material of gas state))

The substrate 1 was set in the vacuum chamber also serving as a measuring device and the voltage was applied to the upper electrode and lower electrodes under an ambience containing gas of benzonitrile at 10⁻⁴ Pa. In step 5, three devices out of the five devices were processed by applying the rectangular waves of the

voltage waveform having the pulse width T1 of 1 ms and the pulse spacing T2 of 10 ms in the pulse waveform of Fig. 6A with the lower electrode side at the higher potential for twenty minutes. After that, the upper electrode side was kept at the higher potential and the voltage was applied for 20 minutes. Further, the current of the devices was monitored at the same time. The voltage was 17 V. The two remaining devices out of the five devices were processed similarly by applying the voltage of 17 V in the pulse waveform of Fig. 6B for 20 minutes.

(Step 6: stabilization step)

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Then the benzonitrile gas was exhausted sufficiently and thereafter the system was evacuated for two hours while being heated at 300 °C.

Then the substrate was set in the vacuum process system of Fig. 5 and the voltage was applied to the lower electrode and upper electrode of each device, and to the anode electrode to measure the currents (the device current and emission current) and the device voltage characteristics. Further, electron beams were observed by luminescence of the fluorescent member placed at the anode. After the measurements, the sample thus formed was then observed with the electron microscope, TEM, and so on.

The device current and emission current both of each device demonstrated the monotonically increasing

characteristics over their threshold. The current was negligible below the threshold (called Vth). Values of emission current of the devices obtained with application of the pulses of Fig. 6A were equivalent to those of the devices obtained with application of the pulses of Fig. 6B and, therefore, their emission efficiencies were also equivalent.

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In observation with the electron emission, the regular pores were observed in the anodic oxide layers. The density of the pores was $1 \times 10^9 \text{ pores/cm}^2$.

Further, cross-sectional samples were prepared and the inside of the pores was observed. The cross sections of the devices were as illustrated in Fig. 17A and Fig. 17B. In Figs. 17A and 17B, the same reference symbols as those in Figs. 12A to 12D denote like portions. Fig. 17A is a cross section of the devices in which carbon was formed by applying the pulses of Fig. 6A in step 5, while Fig. 17B is a cross section of the devices in which carbon was formed by applying the pulses of Fig. 6B in step 5. Numeral 111 indicates the carbon formed on the upper electrode side.

As illustrated in Fig. 17A, where the carbon was formed with application of the pulses of Fig. 6A, the Ni metal was deposited in the columnar shape 110 nm high in the pores from the lower electrode 2 of Al and rim-shape amorphous carbon was further formed along the inner walls of the pores on the top surface of columnar

Ni. Further, amorphous carbon was also formed similarly on the side of the upper electrode 4. A small gap was formed between the carbon on the upper electrode 4 side and the carbon on the lower electrode 2 side and the gap was formed at the edge of the upper electrode. The gap was several nm. The thickness of the anodic oxide film was 150 nm.

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On the other hand, where the carbon was formed with application of the pulses of Fig. 6B, as illustrated in Fig. 17B, the Ni metal was deposited in the columnar shape in the pores on the lower electrode 2 of Al and rim-shape amorphous carbon was further formed along the inner walls of the pores on the top surface of columnar Ni. Further, amorphous carbon was also formed similarly on the side of the upper electrode 4. The carbon was formed to the position 20 nm apart from the bottom surface of the upper electrode and a small gap was formed between the two carbon layers. The gap was several nm.

The above proved the following. First, the rim-shape carbon is formed along the inner walls of the pores, because the deposition rate is controlled under the low partial pressure on the top surface of the columnar metal layer formed in the pores of the anodic oxide layer which is obtained by anodic oxidation of the metal. Second, the small gap of several nm is formed between the carbon films on the upper electrode

side and on the lower electrode side. Third, the emission current and electron emission efficiency are equivalent as long as the small gap is located in the range of 20 nm from the bottom surface of the upper electrode. Since the distance from the gap to the top surface of the upper electrode is 30 nm including the thickness of the upper electrode in the both examples, the probability is assumed to be low of loss of the electrons emitted from the lower electrode side, in the pores. Fourth, the stabilization step enables the device current and emission current to demonstrate the monotonically increasing characteristics without occurrence of the voltage-controlled negative resistance characteristics, or the VCNR characteristics.

[Example 2 of the second embodiment]

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In the present example the substrate was constructed in the device layout similar to Example 1 of the second embodiment. The upper electrode was formed in a variety of thicknesses and influence thereof was investigated. Step 1 to step 3, and step 6 were carried out in the same manner as in Example 1. The description of step 1 to step 3, and step 6 will be omitted herein and only steps 4 and 5 will be described in detail.

(Step 1: step of forming the lower electrodes of metal on the substrate)

This step was carried out in the same manner as step 1 of Example 1.

(Step 2: step of anodizing the lower electrodes)

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This step was carried out in the same manner as step 2 of Example 1.

(Step 3: step of forming columnar metal in the pores of the anodic oxide layers)

This step was carried out in the same manner as step 3 of Example 1.

10 (Step 4: step of forming the upper electrode on the metal or the semiconductor thus anodized)

The upper electrode 72 was formed in either of four thicknesses of 5, 10, 100, and 500 nm on each substrate in the same manner as the lower electrodes, thus forming four substrates.

(Step 5: step of forming carbon in the pores of the anodic oxide layers (under existence of organic material of gas shape))

Each substrate 1 was set in the vacuum chamber also serving as a measuring device and the voltage was applied to the upper electrode and lower electrode under an ambience containing gas of benzonitrile at 10⁻⁴ Pa. Three devices out of the five devices were processed by applying the rectangular waves of the voltage waveform having the pulse width T1 of 1 ms and the pulse spacing T2 of 10 ms in the pulse waveform of Fig. 6A for fifteen minutes with the lower electrode

side at the higher potential. After that, the upper electrode was kept at the higher potential and the voltage was applied for five minutes. At the same time, the current of device was monitored. The voltage was 15 V.

(Step 6: stabilization step)

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This step was carried out in the same manner as step 2 of Example 1.

Next, each substrate was set in the vacuum process system of Fig. 5 and the voltage was applied to the lower electrode and upper electrode of each device, and to the anode electrode to measure the currents (the device current and emission current) and the device voltage characteristics. Further, the electron beam was observed by luminescence of the fluorescent member placed at the anode.

Fig. 18 shows the relation between thickness of the upper electrode and emission efficiency. As shown in Fig. 18, the electron emission efficiency did not decrease below the thickness of about 200 nm and then decreased with increasing thickness of the upper electrode over 200 nm. The electron emission efficiency is defined as a ratio of emission current to device current. Further, the beam size also decreased.

In observation of the form of the upper electrode, particularly, in the case of the upper electrode having the large thickness, where the

thickness was greater than the diameter of the pores, the inside of the pores was also covered in part. When the small gap was observed with section TEM, the small gap was formed at the edge of the bottom surface of the upper electrode in either sample, as in Example 1.

The above verified the following. First, the small gap is formed at the edge of the upper electrode, irrespective of the thickness of the upper electrode. Second, the emission current and electron emission efficiency decrease, depending upon the thickness of the upper electrode. This is assumed to be due to the high probability of loss at the upper electrode of the porous shape, of the electrons emitted from the lower electrode side.

15 [Example 3 of the second embodiment]

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In the present example the substrate was constructed in the device layout similar to Example 1 of the second embodiment. In the present example, SiO₂ was used as the insulating layer instead of the anodic oxide layer of aluminum in Example 1. Production steps of the present example will be described specifically. (Step 1: step of forming the lower electrodes of metal on the substrate)

The substrate 1 was prepared by depositing SiO_2 in the thickness of 1 µm on soda lime glass and then the substrate 1 was washed well with detergent, pure water, and organic solvent or the like. The material

Pt for the lower electrode was deposited in the thickness of 500 nm on the substrate by sputtering and thereafter the lower electrode wires 71 were formed in stripes on the substrate 1 by the photolithography technology.

(Step 2: step of forming the insulating layer)

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 $$\operatorname{\text{Next}},\;\operatorname{SiO_2}$$ was deposited in the thickness of 50 $$\operatorname{\text{nm}}$$ by sputtering.

(Step 3: step of forming the upper electrode on the insulating layer)

The upper electrode 72 was made of Pt in the thickness of 10 nm in the same manner as the lower electrodes were.

(Step 4: step of forming the pores in the insulating layer)

In the stack structure of lower electrode / SiO₂ / upper electrode as described above, four types of pores were formed as follows by the focused ion beam method; (the diameter 50 nm and the pitch 100 nm of the pores), (the diameter 200 nm and the pitch 400 nm of the pores), (the diameter 500 nm and the pitch 1000 nm of the pores), and (the diameter 1000 nm and the pitch 2000 nm of the pores). Here, the pitch is a distance between centers of adjacent pores.

25 (Step 5: step of forming carbon in the pores of the insulating layer (under existence of organic material of gas shape))

The substrate 1 was set in the vacuum chamber also serving as a measuring device and the voltage was applied to the upper electrode and lower electrode under an ambience containing gas of benzonitrile at 10⁻⁴ Pa. The rectangular waves of the voltage waveform having the pulse width T1 of 1 ms and the pulse spacing T2 of 10 ms in the pulse waveform of Fig. 6A were applied for fifteen minutes and then the lower electrode side was kept at the higher potential for five minutes.

(Step 6: stabilization step)

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Then the benzonitrile gas was exhausted sufficiently and thereafter the system was evacuated for two hours while being heated at 300 °C.

Then the substrate was set in the vacuum process system of Fig. 5 and the voltage was applied to the lower electrode and upper electrode of each device, and to the anode electrode to measure the currents (the device current and emission current), and the device voltage characteristics.

The electron emission efficiency was dependent upon the diameter of the pores as illustrated in Fig. 19, and the electron emission efficiency increased with decreasing diameter of pore.

25 [Example 4 of the second embodiment]

The present example is an example of application to the image pickup device of Figs. 9A and

9B described previously, in which a plurality of electron-emitting devices prepared by the same method as in Example 1 of the second embodiment are placed in a two-dimensional array on the substrate.

The production method of the image pickup device of the present example is the same as in the first embodiment. The image pickup device produced in this way was operated based on the principle of operation stated previously, whereupon the signal current was obtained in 1:1 correspondence to the size of the electron-emitting device, thereby verifying the operation.

[Example 5 of the second embodiment]

The present example is an example of construction of the display device of Figs. 10A and 10B described previously, in which a plurality of electron-emitting devices produced by the same method as in Example 1 of the second embodiment are arrayed in a two-dimensional pattern on the substrate. The production method of the display device of the present example is the same as in the first embodiment. The display device produced in this way was operated based on the principle of operation discussed previously, and a bright image was displayed in high definition.

25 [Third Embodiment]

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Fig. 20A is a sectional view of the electronemitting device of the present embodiment. Fig. 20B is a partly enlarged, schematic view of part A in the sectional view of Fig. 20A. The present embodiment is application of the anodic oxide layer to the insulating layer. Figs. 21A to 21D illustrate respective electron-emitting devices having a variety of electron-emitting bodies. Figs. 22A and 22B show other structural examples.

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In Figs. 20A and 20B and Figs. 21A to 21D, numeral 1 denotes a substrate, 2 an upper electrode, 3 an anodic oxide layer, 4 an upper electrode, 5 pores of the porous structure, 6 electron-emitting bodies, and 207 a small gap.

The substrate 1 to be employed herein can be selected from quartz glass, glass with a decreased content of impurity such as Na, soda lime glass, a glass substrate obtained by depositing SiO₂ on soda lime glass by sputtering or the like, ceramics such as alumina, an Si substrate, an Si substrate with a deposited layer of SiO₂, and so on. Particularly, when the substrate 1 is a semiconductor substrate, a driver or the like for driving the electron-emitting device can also be mounted simultaneously.

The lower electrode 2 is selected from metals, such as Al, Ta, Nb, Ti, Zr, Hf, or Si, and semiconductors that can undergo anodic oxidation. The thickness of the lower electrode 2 is properly determined according to the thickness of the anodic

oxide layer, the electrical resistance of the lower electrode, and so on. The materials for the lower electrode are not limited to only the metals that can be anodized, but they may also be of a stack form of a metal that cannot be anodized and a metal that can be anodized.

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The anodic oxide layer 3 is formed by anodic oxidation of the lower electrode in part. In the anodic oxide layer 3 there exist regular or irregular pores 5. This will also be called porous structure in the present specification. The regular or irregular pores 5 can be formed by selecting anodic oxidation conditions including a composition of an anodic oxidation bath, the temperature of the bath, the voltage, the time, etc., according to the material for the lower electrode 2. Preferably, the regular pores are selected. Diameters of the pores range from several ten nm to several hundred nm and depths thereof from several ten nm to several thousand nm. density of the pores is 10^8 to 10^{12} pores/cm². The shape of the pores is not limited only to the circle, but the ellipse, square, etc. can also be applied to the electron-emitting devices of the present invention. The variety of shapes can also be formed using the focused ion beam or the like. Therefore, the expression "length of pore" will also be used in place of the diameter of pore in the present invention.

pore 5 has carbon of an electron-emitting body 6 electrically connected to the lower electrode 2.

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The electron-emitting bodies can be formed in a variety of forms. The upper electrode 4 is kept at the higher potential than the lower electrode 2 is, so as to create a locally high electric field in the electron-emitting bodies, thereby causing electrons to tunnel from the electron-emitting bodies into the vacuum. The above "vacuum" is equivalent to the vacuum ambience in which the substrate with the electron-emitting device formed is set.

Fig. 21A is an example in which needlelike electrodes are provided in the pores. The needlelike electrodes are equivalent to those called the Spindt type stated previously.

Fig. 21B is an example in which small particles are provided in the pores. Grains of the small particles correspond to the tips of the needlelike electrodes of Fig. 21A.

21A and 21B the local electric field is strong and the thickness of the vacuum part is large, the capacitance can be relatively lower than in the structures of Figs. 21C and 21D described below.

25 Fig. 21C is an example in which a high electric field is created in a small gap 207 between a rim-shape conductive body formed along the inner wall of each

pore and the upper electrode to emit electrons. Since the electron-emitting bodies are formed in the rim shape or the linear shape along the inner walls of the pores, the area capable of emitting electrons can be increased considerably, as compared with the structure of Fig. 21A, so that large electron emission current can be obtained.

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Fig. 21D is an example in which the electronemitting bodies 6 are conductive bodies of the columnar
shape formed in the pores and in which a high electric
field is created in a small gap 207 between the
columnar conductive bodies 6 and the upper electrode to
emit electrons. Since the electron-emitting bodies are
of the rim shape or the linear shape along the inner
walls of the pores, the area capable of emitting
electrons can be increased considerably, as compared
with the structure of Fig. 21A, so that large electron
emission current can be obtained.

The upper electrode is formed on the anodic oxide layer, and the electron-transmitting portions above the pores are preferably made of a conductive material with excellent electron transmission characteristics and heat resistance and particularly preferably made of carbon or the like. Here, the "carbon" means a carbon material having at least one of graphite, amorphous carbon, and diamondlike carbon.

In order that the upper electrode can cover the

apertures of the pores, the thickness of the upper electrode is set to be not less than $0.5 \times L$ where L is the length of the pores.

Letting λ stand for the mean free path of transmission of electrons, the thickness of the upper electrode is not more than 2λ for efficient transmission. In general, electron transmittance T is expressed by the following.

 $T = Aexp (-t/\lambda)$

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In the above equation, A represents a constant and t the thickness of the upper electrode. From the above equation, the transmittance of not less than 10 % of injected electrons can be expected if the thickness of the upper electrode is not more than 2λ . In the above equation, the mean free path λ can be calculated from dependence of emission current on the thickness of the upper electrode.

For example, in the case of the carbon, which is the particularly preferred material in the present invention, the above requirements simultaneously determine preferred ranges for the thickness of the upper electrode and for the length of the pores; for example, when the thickness of the upper electrode is 50 nm, the length of the pores is not more than 100 nm.

The thickness of the upper electrode on the insulating layer may be different from the thickness of the upper electrode portions that transmit electrons

above the pores and they are properly determined from the needs in the production process and the like.

The other structural examples of the electronemitting device of the present invention will be
described using the schematic sectional views of Figs.

22A and 22B. As the structure of the electron-emitting
bodies 6, the example of Fig. 21A will be used, but,
without having to be limited to this structure, either
one of the structures of the electron-emitting bodies
of Figs. 21B, 21C, 21D, etc. can also be employed.

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Fig. 22A is an example in which the conductive bodies 8 of the columnar shape and the electron-emitting bodies 6 are provided in the pores. In this case, existence of the conductive bodies 8 decreases the resistance of the region from the lower electrode to the electron-emitting bodies, so that the insulating layer can be formed in a sufficiently large thickness. This can decrease the capacitance between the lower electrode and the upper electrode, which is advantageous in driving.

Fig. 22B is an example in which an insulating layer of a thickness permitting tunneling is provided between the lower electrode 2 and the electron-emitting bodies 6 in the pores, thereby forming a nonlinear device of metal/insulating layer/ carbon. This structure imparts the function of current limitation. This structure can prevent current fluctuation due to

discharge or the like and in turn prevent damage to the electron-emitting device during driving of the electron-emitting device of the present invention. A specific production method for producing the insulating metal oxide layer in the thickness permitting tunneling will be described hereinafter.

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There are a variety of methods for producing the above electron-emitting device, among which an example is schematically illustrated in the production step diagram of Fig. 23. An example of the production method of the electron-emitting device of Fig. 21D will be described referring to Fig. 23.

(Step 1) Step of forming the lower electrode of the metal or the semiconductor on the substrate

The substrate 1 is cleaned well with detergent, pure water, and organic solvent or the like, the material for the lower electrode is deposited by vacuum evaporation, sputtering, or the like, and thereafter the lower electrode 2 is formed on the substrate, for example, by the photolithography technology. The lower electrode may also be formed by electrolytic crystallization.

(Step 2) Step of anodizing the lower electrode

The anodic oxidation system will be first

described herein using the conceptual drawing thereof
illustrated in Fig. 15. Numeral 51 denotes an anodic
oxidation tank, 52 an anodic oxidation electrolyte

solution, 53 an electrode, 54 an anodic oxidation power supply, 55 a temperature controller for controlling the temperature of the anodic oxidation electrolyte solution 52, 56 a vessel for water circulating in the temperature controller, and 57 the circulating water for control of temperature.

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The anodic oxidation electrolyte solution 52 for the metal such as Al is an aqueous solution of one selected from inorganic acids such as sulfuric acid, sulfamic acid, and phosphoric acid, and organic acids such as oxalic acid, malonic acid, and succinic acid, and the substance added thereto as solvent is polyhydric alcohol such as ethylene glycol, glycerin, or dextrin. On the other hand, the electrolyte solution for Si is an aqueous solution of HF. Further, an oxidation process such as thermal oxidation may be further added.

The electrode 53 is the metal such as Pt. The anodic oxidation of the lower electrode is effected by energization from the power supply 54 with the electrode 53 as a cathode and the substrate 1 as an anode. The geometrical structure of the anodic oxide layer can be controlled by production conditions. Specifically, the spacing between the pores can be controlled by the anodic oxidation voltage, the depths of the pores by the anodic oxidation time, and the diameters of the pores by such conditions as the

composition of the electrolyte solution, the voltage, the current. Further, control of the regular pores or the irregular pores can also be made by control of these conditions.

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Next, the substrate with the anodic oxide layer formed thereon is dipped in the anodic oxidation electrolyte solution or the like to adjust the diameter of the pores and the thickness of the dense oxide film. (This step will be called widening.) Then the substrate is washed well with water and then dried in vacuum.

(Step 3) Step of forming the upper electrode on the metal or the semiconductor thus anodized

The upper electrode is formed in the thickness of several nm to several ten nm in the same manner as the lower electrode was.

(Step 4) Step of forming the electron-emitting bodies in the pores of the anodic oxide layer (under existence of organic material of gas state)

This step is a step of forming carbon in the pores of the aforementioned anodic oxide layer by applying the voltage to the upper electrode and lower electrode under existence of the organic material of a gas state. The carbon formed in this step is, for example, graphite (including so-called HOPG, PG, and GC). HOPG indicates the almost perfect graphite crystal structure, PG somewhat disordered crystal

structure having crystal grains of 20 nm or so, and GC more disordered crystal structure having the crystal grains of 2 nm or so. In addition, the carbon may also be non-crystalline carbon (which means amorphous carbon and, a mixture of amorphous carbon with fine crystals of the aforementioned graphite). Accordingly, the carbon is one similar to the upper electrode as described above.

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The preferred gas pressure of the organic substance for formation of the carbon differs depending upon the aforementioned application form, the shape of the vacuum vessel, the type of the organic substance, and so on and is thus properly determined according to the circumstances. An appropriate organic substance can be selected from aliphatic hydrocarbons of alkane, alkene, and alkyne, aromatic hydrocarbons, alcohols, aldehydes, ketones, amines, organic acids such as phenol, carboxylic acid, and sulfonic acid, and so on. Specific examples of such substances include saturated hydrocarbons represented by C_nH_{2n+2} such as methane, ethane, and propane, unsaturated hydrocarbons represented by the composition formula of C,H2, or the like such as ethylene and propylene, benzene, toluene, methanol, ethanol, formaldehyde, acetaldehyde, acetone, methyl ethyl ketone, methylamine, ethylamine, phenol, formic acid, acetic acid, propionic acid, and so on.

The organic gas is also selected according to

the diameter of the pores formed in the anodic oxide layer. This is because adsorption of the organic gas is also dependent on the diameter of the pores.

During this process carbon is deposited from the organic substance present in the ambience into the pores in the anodic oxide layer, whereby the device current If and emission current Ie change remarkably.

Completion of this step is determined while measuring either one of the device current If and the emission current Ie or the both.

The apertures of the upper electrode 4 above the pores can also be formed in the initial stage of application of the above voltage pulses in this step.

(Step 5) Stabilization step

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This step is a step for stabilizing the characteristics of the electron-emitting device thus produced. This step is necessary, particularly, where the formation of the electron-emitting bodies is carried out according to step 4) described above. This step is a step of removing intermediate products of the organic material and also removing the organic gas, water, oxygen, etc. adsorbing to the substrate etc. from the carbon in the pores of the anodic oxide layer in the above step, whereby the step can impart to the device such a property that the device current and the emission current monotonically increase above a certain threshold against the voltage applied to the device.

This step is a step of exhausting the organic substance in the vacuum vessel and the evacuation apparatus for evacuating the vacuum vessel is preferably one not using oil in order to avoid influence of the oil from the apparatus on the characteristics of the device.

Specifically, the evacuation apparatus can be selected from a sorption pump, an ion pump, and so on.

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The partial pressure of the organic component in the evacuation apparatus is set to a partial pressure under which there is little carbon or carbon compound newly deposited, and is preferably not more than 1 \times 10⁻⁸ Torr and particularly preferably not more than 1 \times 10⁻¹⁰ Torr. It is further preferred that the whole of the vacuum apparatus be heated during evacuation of the inside of the vacuum apparatus so as to facilitate removal of molecules of the organic substance adsorbing to the inner wall of the vacuum apparatus and to the electron-emitting device. The heating condition at this time is desirably the temperature of 150 to 300 °C and the heating time of not less than several hours, but the heating condition is not limited particularly to this condition.

The ambience during driving after completion of the stabilization step is preferably maintained in the ambience at the end of the above stabilization operation, but it is not limited to this. Sufficient characteristics can be maintained by an ambience from

which the organic substance is removed adequately but the vacuum degree of which is a little degraded.

By employing such a vacuum ambience, deposition of new carbon substance can be suppressed, whereby the device current If and emission current Ie are stabilized as a result.

(Step 6) Step of forming the upper electrode 4

Using a target of graphite, amorphous carbon,
or the like, graphite, amorphous carbon, or the like is
deposited on the pores and on the upper electrode 4 by
sputtering or the like.

Further, the stabilization step of step 5 is carried out, whereby the purpose of the above step 5 is further accomplished.

15 [Example 1 of the third embodiment]

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The electron-emitting devices were produced in the same structure as in Figs. 7A and 7B. Production steps of the present example will be described specifically.

20 (Step 1: step of forming the lower electrodes of metal on substrate)

The substrate 1 was prepared by depositing SiO_2 in the thickness of 1 μm on soda lime glass and the substrate 1 was washed well with detergent, pure water, and organic solvent or the like. Then the material of Al for the lower electrodes was deposited in the thickness of 500 nm on the substrate by sputtering and

thereafter the lower electrode wires 81 were formed in stripes on the substrate 1 by the photolithography technology. For using parts of the lower electrode wires 81 as terminals, they were covered with a known mask resin for plating.

(Step 2: step of anodizing the lower electrodes)

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Using the apparatus of Fig. 15, the anodic oxidation was carried out to anodize parts of the Al lower electrodes prepared in (step 1).

10 The anodic oxidation electrolyte solution 52 was an aqueous solution of oxalic acid 30 g/l. electrode 53 was a Pt electrode. The anodic oxidation was carried on at 5 °C for five minutes by the constant voltage of 40 V from the power supply 55 with the 15 cathode of the electrode 53 and the anode of the lower wires 81 provided on the substrate 1. On this occasion, the initial current density was 300 mA/cm2, but the current density decreased with progress of the anodic oxidation and thereafter increased once to be 20 saturated. Then the substrate with the anodic oxide layers was immersed in an aqueous solution of phosphoric acid for thirty minutes to remove the dense anodic oxide layer and thereafter washed well with water.

25 (Step 3: step of forming columnar metal in the pores of the anodic oxide layers)

Formation of the columnar metal in the pores

was carried out using the apparatus of Fig. 16. In Fig. 16, portions with the same reference numerals as those in Fig. 15 indicate like portions. Numeral 91 represents a counter electrode for electrolytic deposition of metal, which is a counter electrode made of an inactive electrode such as carbon or Pt, or the same material as the electrodeposited metal. Numeral 92 indicates a container for a metal electrodeposition liquid, 93 a power supply for electrodeposition, and 94 an electrodeposition solution containing the metal.

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In this step Ni was electrodeposited by the constant current at the current density of 1 mA/cm², using the Pt electrode as the counter electrode 91 and 5 % NiSO4 and 4 % H3BO3 as the electrodeposition solution 94 containing the metal. An electrodeposition amount of columnar Ni was controlled by time and the columnar Ni was formed in each pore. The electrodeposition time was 100 seconds.

(Step 4: step of forming the upper electrode on the

The upper electrode 82 was made of Pt in the thickness of 10 nm in the same manner as the lower electrodes were.

(Step 5: step of forming carbon in the pores of the anodic oxide layers (under existence of organic material of gas state))

metal or the semiconductor thus anodized)

The substrate 1 was set in the vacuum chamber

also serving as a measuring device and the voltage was applied to the upper electrode and lower electrodes under an ambience containing gas of acetone at 10⁻¹ Pa. In step 5, the rectangular waves of the voltage waveform having the pulse width T1 of 1 ms and the pulse spacing T2 of 10 ms in the pulse waveform of Fig. 6A were applied for twenty minutes with the lower electrode side at the higher potential. After that, the upper electrode side was kept at the higher potential and the voltage was applied for 20 minutes. Thereafter, the system was evacuated and the substrate was taken out.

(Step 6: stabilization step)

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Then the substrate was set in the vacuum chamber of the sputtering apparatus and the chamber was evacuated well. Thereafter, the chamber was evacuated for two hours while being heated at 300 °C.

(Step 7: step of forming the upper electrode)

Next, with a target of graphite, carbon was deposited in the thickness of 45 nm by sputtering, thereby forming the upper electrode.

Then the substrate was set in the vacuum process system of Fig. 5 and the voltage was applied to the lower electrode and upper electrode of each device, and to the anode electrode to measure the currents (the device current and emission current), and the device voltage characteristics. The electron beam was

observed by luminescence of the fluorescent member set at the anode. After the measurements, the sample thus formed was then observed with the electron microscope, TEM, and so on.

5 [Comparative Example]

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An MIM type electron-emitting device was produced as a comparative example.

The following steps were carried out; (step 1: step of forming the lower electrode of metal on the substrate), (step 2: step of anodizing the lower electrode), and (step 4: step of forming the upper electrode on the metal or the semiconductor thus anodized). Steps 1 and 4 are the same as in the example, but the anodic oxidation conditions of step 2 were changed. The anodic oxidation conditions were as follows; the anodic oxidation solution was an ammonium tartrate solution, constant current anodic oxidation was carried out at 500 μ A/cm², and the thickness of the insulating layer was 6 nm.

Each device demonstrated the monotonically increasing characteristics for both the device current and the emission current over their threshold. The current was negligible below the threshold (Vth). When the electron beam was observed by luminescence of the fluorescent member, it was equivalent to that of the MIM electron-emitting device of the comparative example. The electron emission efficiency of the

comparative example was 0.1 %, whereas that of the example was 5 % on average. At the same time, the electron emission current increased corresponding to the efficiency.

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In observation of cross section with the electron microscope, the regular pores were observed in the anodic oxide layers. The diameter of the pores was 80 nm. The polelike Ni metal and carbon were stacked in the pores and there was the small gap of 5 to 10 nm with respect to the upper electrode.

The above verified that the spread of electron beam was equivalent to that of the MIM electron-emitting devices and that the electron-emitting devices demonstrated high electron emission efficiency and emission current. Thanks to the stabilization step, both the device current and emission current showed the monotonically increasing characteristics having the threshold Vth without occurrence of the voltage-controlled negative resistance characteristics, or the VCNR characteristics.

[Example 2 of the third embodiment]

In the present example the substrate was constructed in the device layout similar to Example 1 of the third embodiment. In the present example, the anodic oxidation conditions of aluminum and the diameter of the pores in Example 1 were changed and influence thereof was investigated.

(Step 1: step of forming the lower electrodes of metal on the substrate)

This step was carried out in the same manner as step 1 of Example 1.

5 (Step 2: step of anodizing the lower electrodes)

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This step was carried out in the same manner as step 2 of Example 1.

Next, the diameters of the pores were changed by changing the time for which the substrate with the anodic oxide layers formed therein was immersed in the aqueous solution of phosphoric acid. The diameters of the pores were 20, 30, 40, 50, and 80 nm.

(Step 3: step of forming columnar metal in the pores of the anodic oxide layers)

was carried out using the apparatus of Fig. 16. In this step, Ni was electrodeposited using the Pt electrode as the counter electrode 91, 5 % NiSO₄ and 4 % H₃BO₃ as the electrodeposition solution 94 containing the metal, and the alternating current of 60 Hz at the current density of 1 mA/cm². An electrodeposition amount of columnar Ni was controlled by time and columnar Ni was formed in each pore. Ni also migrated into the dense oxide layer at the bottom of the pores of the anodic oxide layers, so that the columnar Ni was electrically connected to the lower electrode.

(Step 4: step of forming the upper electrode on the

metal or the semiconductor thus anodized)

This step was not carried out.

(Step 5: step of forming the electron-emitting bodies in the pores of the anodic oxide layers)

A layer of W was deposited in the thickness of 7 nm by sputtering and thereafter reduced and aggregated in hydrogen gas, thereby forming small particles thereof. The grain size of the small particles was 10 nm.

10 (Step 6: stabilization step)

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Next, the substrate was set in the vacuum chamber of the sputtering apparatus and the chamber was evacuated well.

(Step 7: step of forming the upper electrode)

Next, with a target of graphite, carbon was deposited in the thickness of 20 nm by sputtering, thereby forming the upper electrode.

According to observation with the electron microscope, the carbon was also able to cover the regions above the pores as long as the diameter of the pores was below 40 nm; the carbon above the pores failed to cover parts or the whole of the regions above the pores if the diameter of the pores was not less than 50 nm. This proved that the thickness t of the upper electrode needs to satisfy the following condition against the length L of the pores:

 $0.5 \times L \leq t$.

In the same manner as the example, it was verified that the devices having the pore diameters not more than 40 nm were able to emit electrons in the beam spread equivalent to that of the comparative example.

5 [Example 3 of the third embodiment]

on the substrate)

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In the present example the substrate was constructed in the device layout similar to Example 1 of the third embodiment. In the device structure of Fig. 21B, samples were formed with a variety of thicknesses of the upper electrode and influence thereof was investigated. The same steps as in Example 1 were carried out except for steps 5 and 7.

(Step 1: step of forming the lower electrodes of metal

This step was carried out in the same manner as step 1 of Example 1.

(Step 2: step of anodizing the lower electrodes)

This step was carried out in the same manner as step 2 of Example 1.

20 (Step 3: step of forming columnar metal in the pores of the anodic oxide layers)

This step was carried out in the same manner as step 3 of Example 1.

(Step 4: step of forming the upper electrode on the metal or the semiconductor thus anodized)

This step was carried out in the same manner as step 4 of Example 1.

(Step 5: step of forming the electron-emitting bodies in the pores of the anodic oxide layers)

W was deposited in the thickness of 7 nm by sputtering and thereafter reduced and aggregated in hydrogen gas, thereby forming small particles thereof. (Step 6: stabilization step)

Then the substrate was set in the vacuum chamber of the sputtering apparatus and the chamber was evacuated well. After that, the chamber was evacuated for two hours while being heated at 300 °C.

(Step 7: step of forming the upper electrode)

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Next, with a target of graphite, the carbon was deposited in either thickness of 10, 35, 50, 65, 80, and 200 nm by sputtering, thereby forming the upper electrode.

Then the substrate was set in the vacuum process system of Fig. 5 and the voltage was applied to the lower electrode and upper electrode of each device, and to the anode electrode to measure the currents (the device current and emission current), and the device voltage characteristics. Further, the electron beam was observed by luminescence of the fluorescent member placed at the anode.

The electron beam was more spread in the device of the thickness of 10 nm than in the comparative example. The devices having the thicknesses of 35, 50, 65, and 80 nm were equivalent to the comparative

example. With the device having the thickness of 200 nm, the emission current was too small to measure.

As illustrated in Fig. 24, the electron emission current was very high at the upper electrode thickness of 10 nm and showed exponential dependence in the range of 35, 50, 65, and 80 nm. The current at the thickness of 200 nm was of the noise level. The mean free path of carbon was calculated based on this result.

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10 According to observation of the forms of the upper electrodes, the upper electrode failed to cover the regions above the pores in the samples of the thicknesses of 10 and 35 nm and holes were observed in the upper electrode. There were no holes observed in the regions above the pores in the samples having the thicknesses of 50, 65, and 80 nm.

The above results verified the following. There is an optimum value of the thickness of the upper electrode against the diameter of the pores. If the upper electrode is too thin, the upper electrode will fail to cover the pores and the electron beam will spread. Within the optimum range, the spread of beam is decreased and the emission current decreases depending upon the thickness. Further, sufficient emission current can be obtained if the upper electrode has the thickness not more than 2λ as described previously.

[Example 4 of the third embodiment]

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The present example is an example of application to the image pickup device of Figs. 9A and 9B described previously, in which a plurality of electron-emitting devices prepared by the same method as in Example 1 of the third embodiment are placed in a two-dimensional array on the substrate.

The production method of the image pickup device of the present example is the same as in the first embodiment. The image pickup device produced in this way was operated based on the principle of operation stated previously, whereupon the signal current was obtained in 1:1 correspondence to the size of the electron-emitting device, thereby verifying the operation.

[Example 5 of the third embodiment]

The present example is an example of construction of the display device of Figs. 10A and 10B described previously, in which a plurality of electron-emitting devices produced by the same method as in Example 1 of the third embodiment are arrayed in a two-dimensional pattern on the substrate. The production method of the display device of the present example is the same as in the first embodiment. The display device produced in this way was operated based on the principle of operation discussed previously, and a bright image was displayed in high definition.

[Fourth Embodiment]

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Fig. 25A is a sectional view of the electronemitting device of the fourth embodiment. Fig. 25B is a partly enlarged schematic view of part A in the sectional view of Fig. 25A.

The substrate 1 to be employed herein can be selected from quartz glass, glass with a decreased content of impurity such as Na, soda lime glass, a glass substrate obtained by depositing SiO₂ on soda lime glass by sputtering or the like, ceramics such as alumina, an Si substrate, an Si substrate with a deposited layer of SiO₂, and so on. Particularly, when the substrate 1 is a semiconductor substrate, a driver or the like for driving the electron-emitting device can also be mounted simultaneously.

The lower electrode 2 is selected from metals, such as Al, Ta, Nb, Ti, Zr, Hf, or Si, and semiconductors that can undergo anodic oxidation. The thickness of the lower electrode 2 is properly determined according to the thickness of the anodic oxide layer, the electrical resistance of the lower electrode, and so on. The materials for the lower electrode are not limited to only the metals that can be anodized, but they may also be of a stack form of a metal that cannot be anodized and a metal that can be anodized.

The anodic oxide layer 3 is formed by anodic

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oxidation of the lower electrode in part. In the anodic oxide layer 3 there exist regular or irregular pores 5. This will also be called porous structure in the present specification. The regular or irregular pores 5 can be formed by selecting anodic oxidation conditions including a composition of an anodic oxidation bath, the temperature of the bath, the voltage, the time, etc., according to the material for the lower electrode 2. Preferably, the regular pores are selected. Diameters of the pores range from several ten nm to several hundred nm and depths thereof from several ten nm to several thousand nm. density of the pores is 10^8 to 10^{12} pores/cm². The shape of the pores is not limited only to the circle, but the ellipse, square, etc. can also be applied to the electron-emitting devices of the present invention. The variety of shapes can also be formed using the focused ion beam or the like. Therefore, the expression "length of pore" will also be used in place of the diameter of pore in the present invention. each pore 5 the carbon 6 electrically connected to the lower electrode 2 is formed in the polelike shape filling a part of the pore. Electrons are emitted from the peripheral part of the pole in each pore or from the region of the top surface of the pole and the emission of electrons is determined by the shape of the pole and the shape of the upper electrode on the anodic

oxide layer. Accordingly, electrons are emitted in a linear shape or in a linear and surface shape from each pore, according to the pore.

The carbon may also be formed in the similar fashion from the side of the upper electrode 4.

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There is a gap created between the carbon formed on the lower electrode 2, and the upper electrode or, in the case where the carbon is also formed from the side of the upper electrode 4, between the carbon from the upper electrode 4 side and the carbon formed on the lower electrode 2. This gap is preferably several nm to several ten nm, and is properly determined according to the time of the step of applying the voltage to the upper electrode and lower electrode under existence of the organic material described hereinafter, the voltage applied, and so on.

The upper electrode is formed above the anodic oxide layer and is made preferably of a material having a high melting point, such as Pt, W, Mo, or Hf.

Structural examples of the above electronemitting device of the present invention will be
explained using the schematic sectional views of Figs.
26A and 26B. In Figs. 26A and 26B, numeral 207
designates a small gap and the same portions as in
Figs. 25A and 25B are denoted by the same reference
numerals. There are two kinds of structures
illustrated in Figs. 26A and 26B, but other structures

may also be employed, without having to be limited to these illustrated structures. The following describes examples using the metal for the upper electrode and the lower electrode, but they may also be made of the semiconductor.

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The structure of Fig. 26A is metal (lower electrode) / metal oxide layer / pores, each having a carbon electron-emitting body 6 / vacuum / metal (upper electrode) 4 formed in the regions except for the regions above the pores. The structure of Fig. 26B is metal (lower electrode) / pores, each having an electron-emitting body 6 / vacuum / metal (upper electrode) 4 formed in the regions except for the regions above the pores.

In the structure of Fig. 26A, the metal oxide layer 3 is obtained on the occasion of anodic oxidation of the lower electrode, and two structural regions, a dense film structural region without pores and a film structural region with pores, can be obtained in this metal oxide layer 3, depending upon the anodic oxidation conditions. As illustrated in Fig. 26A, the formation of the dense film structural region of the above metal oxide layer between the lower electrode 2 and the electron-emitting bodies 6 in the pores results in forming a nonlinear device in the structure of metal / insulator / carbon, so as to impart the function of current limitation, which can prevent the current

fluctuation in discharge or the like on the occasion of driving the electron-emitting device of the present invention and which can in turn prevent damage to the electron-emitting device. A specific production method of the above metal oxide layer will be described hereinafter, but it is first formed, for example, under conditions for forming the porous metal oxide and thereafter the thickness of the dense film structural region is adjusted in the widening step of pores described hereinafter.

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The structure of Fig. 26B does not have the metal oxide layer without the pores and the electronemitting bodies (carbon) in the pores are electrically connected directly to the lower electrode. structure is constructed by anodizing the lower electrode, thereafter sufficiently widening the pores by the widening step of pores described hereinafter, and further forming the electron-emitting bodies (carbon) in the pores, whereby the lower electrode becomes electrically connected to the electron-emitting bodies in some cases. On this occasion, the metal oxide layer without the pores between the lower electrode and the metal oxide layer with the pores may be electrically broken by the pulse voltage applied in the step of forming the carbon in the pores of the anodic oxide layer described hereinafter, so that the electron-emitting bodies are electrically connected to

the lower electrode. In the structure of Fig. 26B, the electron-emitting device is also provided with the nonlinear characteristics by tunneling between the electron-emitting bodies and the vacuum. The electrical connection with the lower electrode can also be achieved in such a way that the metal is precipitated by alternating current into the pores of the anodic oxide film by the coloring method of the anodic oxide film conventionally well known whereupon the precipitating metal into the pores migrates into the dense anodic oxide film to implement the electrical connection. The above "vacuum" is one equivalent to the vacuum ambience in which the substrate with the electron-emitting device formed thereon is set.

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In the electron-emitting device of the present invention described above, the carbon making the electron-emitting bodies is preferably at least one of graphite, amorphous carbon, and diamondlike carbon, particularly, in terms of heat resistance, stability of electron emission characteristics, and improvement in repeatability, as stated previously.

Next described is an electron-emitting mechanism of the electron-emitting device of the present invention in the structural examples of Fig. 26A and Fig. 26B.

In the surface conduction electron-emitting device stated previously in the related background art,

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according to Japanese Laid-open Patent Application No. 9-082214, electrons are once emitted into the vacuum outside the anode from a certain position on the anode side (which is also called the higher potential side) of the fissure region, in the fissure region of the surface conduction electron-emitting device. electrons once emitted move in the electric field created by the cathode (which is also called the lower potential side) and the anode, and electrons flying over the singular point (hereinafter referred to as a stagnation point) of the electric field are attracted to the anode plate by the electric field created by the voltage applied to the anode plate set opposite to the electron-emitting device with intervention of vacuum. The electrons that do not reach the singular point of the electric field drop onto the anode, and some of electrons are scattered here to be deflected and again emitted into the vacuum. Electrons moving over the singular point of the electric field as a result of repetition of this scattering also reach the anode plate.

It is described in the prior art application that, in order to largely increase the electron emission efficiency, the electric field needs to be set in such conditions that most of the electrons once emitted are attracted to the anode plate without dropping onto the anode in the above mechanism of

electron emission and that the electron emission efficiency can be increased by providing the field correcting electrode outside the device electrode and applying a sufficiently higher voltage thereto than the voltage applied to the device for emission of electron.

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In contrast with it, in the case of the electron-emitting device of the present invention, when the higher potential is applied to the upper electrode and the lower potential than that to the upper electrode is applied to the lower electrode, a potential difference between them is placed in the small gap between the upper electrode 4 and the electron-emitting body 6, whereupon electrons are emitted from the electron-emitting bodies into the vacuum. Since a strong electric field is placed in the small gap corresponding to the fissure of the aforementioned prior art, the electrons emitted from the electron-emitting bodies 6 into the vacuum collide with the upper electrode 4 to be scattered, just as in the case of the surface conduction electron-emitting device described previously in the related background art. It is, however, assumed that, in the case of the electron-emitting device of the present invention, the electrons reach the anode plate over the singular point of the electric field without repetition of scattering.

Now, the principle of the electron-emitting device of the present invention will be described using

Fig. 27. Fig. 27 is a diagram to explain the principle of the electron-emitting device of the present invention. In the figure, h indicates the distance between the electron-emitting device and the anode electrode, d the length of pore, and Va the potential of the anode electrode.

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Here, the following discussion is made with focusing attention on electrons emitted from the side of the upper electrode 4 of the electron-emitting body 6 on one side. Since the electrons are emitted along the periphery of the pore from the electron-emitting body 6, the electrons are also emitted from the upper The electrode opposed to the upper electrode 4. electrons emitted from the electron-emitting body 6 into the vacuum collide with the upper electrode 4 because of the electric field placed in the small gap 207 to be first scattered isotropically. Since the strong electric field from the opposite upper electrode present at the very close distance considerably constricts the stagnation point described above, as compared with that in the conventional surface conduction electron-emitting device, the electrons scattered isotropically reach the anode plate without repetitive scattering, mostly after scattered only once. On the other hand, where the thickness of the upper electrode 4 is small, the electrons also reach the anode plate, mostly after scattered only once,

without repetitive scattering. It is considered that the above accounts for the increase of the electron emission efficiency. On the other hand, the same can also be applied to the electron-emitting bodies 6 having the electron-emitting regions formed in the rim shape of the pores, and this is conceivably the cause of increase of the electron emission efficiency.

An important factor for the effect of the electric field of the opposite upper electrode is the diameter of the aperture. Supposing the work function of the electron-emitting body is 4 to 5.5 eV, the electric field for emission of electrons into the small gap is not less than 10⁷ V/cm. When the stagnation point being the singular point of the electric field as defined in the aforementioned prior art is applied to the prior art electron-emitting device and the present invention, the distance Xs of the stagnation point without 34 is represented by the following equation.

$$Xs = h \cdot Vf/(\pi \cdot Va)$$

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On the other hand, the stagnation point Xs' with 34 is indicated by the following equation.

$$Xs' = h \cdot Vf/\{\pi \cdot Va + h \cdot Vf/(\pi \cdot d)\}$$

Therefore, the smaller the diameter of the aperture, the more the stagnation point is constricted.

Particularly, from the reason that the constriction effect of the stagnation point can be expected even at the upper electrode voltage of several ten V, the

diameter of the aperture is preferably not more than 0.5 µm and more preferably not more than 0.2 µm. Further, the thickness of the upper electrode is preferably as thin as possible in order to suppress the repetitive scattering and, from examples, the thickness is preferably not more than 0.2 µm in terms of the efficiency. For specifying the condition by the thickness of the upper electrode, the small gap contributing to the emission of electrons has to be present at the edge of the upper electrode. From the viewpoint of suppressing the repetitive scattering, it corresponds to the distance from the small gap to the upper surface of the upper electrode.

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The driving voltage is a low driving voltage, because the gap is small. Since the direction of the voltage to draw the electrons is coincident with the direction toward the anode plate, a spread of the electron beam, though scattered isotropically, is suppressed relatively.

There are a variety of methods for producing the electron-emitting device described above, among which a first production method will be described referring to the production step diagram of Fig. 28.

(Step 1) Step of forming the lower electrode of the metal or the semiconductor on the substrate

The substrate 1 is cleaned well with detergent, pure water, and organic solvent or the like, the

material for the lower electrode is deposited by vacuum evaporation, sputtering, or the like, and thereafter the lower electrode 2 is formed on the substrate, for example, by the photolithography technology. The lower electrode may also be formed by electrolytic crystallization.

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(Step 2) Step of anodizing the lower electrode The conceptual drawing of the anodic oxidation system was already described referring to Fig. 15. electrode 53 is the metal such as Pt. The anodic oxidation of the lower electrode is effected by energization from the power supply 54 with the electrode 53 as a cathode and the substrate 1 with the lower electrode formed thereon, as an anode. geometrical structure of the anodic oxide layer can be controlled by production conditions. Specifically, the spacing between the pores can be controlled by the anodic oxidation voltage, the depths of the pores by the anodic oxidation time, and the diameters of the pores by such conditions as the composition of the electrolyte solution, the voltage, the current. Further, control of the regular pores or the irregular pores can also be made by control of these conditions.

Next, the substrate with the anodic oxide layer formed thereon is dipped in the anodic oxidation electrolyte solution or the like to adjust the diameter of the pores and the thickness of the dense oxide film.

(This step will be called widening.) Then the substrate is washed well with water and then dried in vacuum.

(Step 3) Step of forming the upper electrode on the metal or the semiconductor thus anodized

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The upper electrode is formed in the thickness of not more than 200 nm in the same manner as the lower electrode was.

(Step 4) Step of forming the electron-emitting bodies in the pores of the anodic oxide layer (under existence of organic material of gas state)

This step is a step of forming carbon in the pores of the aforementioned anodic oxide layer by applying the voltage to the upper electrode and lower electrode under existence of the organic material of a gas state. The carbon formed in this step includes, for example, graphite (including so-called HOPG, PG, and GC). HOPG indicates the almost perfect graphite crystal structure, PG somewhat disordered crystal structure having crystal grains of 20 nm or so, and GC more disordered crystal structure having the crystal grains of 2 nm or so. In addition, the carbon may also be non-crystalline carbon (which means amorphous carbon and, a mixture of amorphous carbon with fine crystals of the aforementioned graphite). The vacuum process system used in this step was already described referring to Fig. 5.

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Particularly, where the carbon of the electronemitting bodies is deposited from the lower electrode so as to form a constant gap with respect to the upper electrode, the carbon can be formed by applying the voltage with the upper electrode at the lower potential and the lower electrode at the higher potential. After the voltage is applied with the upper electrode at the lower potential and the lower electrode at the higher potential, the voltage is further applied with the upper electrode at the higher potential and the lower electrode at the lower potential, whereby the carbon is also deposited on the upper electrode after formation of a constant gap above the deposition of carbon of the electron-emitting bodies from the lower electrode, thereby forming a constant separation from the upper electrode. Since the position of the gap affects the electron emission characteristics as described previously, it is preferable to deposit the carbon from the lower electrode and then form the constant gap from the upper electrode.

The preferred gas pressure of the organic substance for formation of the carbon differs depending upon the aforementioned application form, the shape of the vacuum vessel, the type of the organic substance, and so on and is thus properly determined according to the circumstances. An appropriate organic substance can be selected from aliphatic hydrocarbons of alkane,

alkene, and alkyne, aromatic hydrocarbons, alcohols, aldehydes, ketones, amines, organic acids such as phenol, carboxylic acid, and sulfonic acid, and so on. Specific examples of such substances include saturated hydrocarbons represented by C_nH_{2n+2} such as methane, ethane, and propane, unsaturated hydrocarbons represented by the composition formula of C_nH_{2n} or the like such as ethylene and propylene, benzene, toluene, methanol, ethanol, formaldehyde, acetone, methyl ethyl ketone, methylamine, ethylamine, phenol, formic acid, acetic acid, propionic acid, and so on. The organic gas is also selected according to the diameter of the pores formed in the anodic oxide layer. This is because adsorption of the organic gas is also dependent on the diameter of the pores.

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During this process carbon is deposited from the organic substance present in the ambience into the pores in the anodic oxide layer, whereby the device current If and emission current Ie change remarkably.

Completion of this step is determined while measuring either one of the device current If and the emission current Ie or the both.

The apertures of the upper electrode 4 above the pores, as illustrated in Figs. 26A and 26B, can also be formed in the initial stage of application of the above voltage pulses in this step.

(Step 5) Stabilization step

This step is a step for stabilizing the characteristics of the electron-emitting device thus This step is a step of removing intermediate produced. products of the organic material and also removing the organic gas, water, oxygen, etc. adsorbing to the substrate etc. from the carbon in the pores of the anodic oxide layer in the above step, whereby the step can impart to the device such a property that the device current and the emission current monotonically increase above a certain threshold against the voltage applied to the device. This step is a step of exhausting the organic substance in the vacuum vessel and the evacuation apparatus for evacuating the vacuum vessel is preferably one not using oil in order to avoid influence of the oil from the apparatus on the characteristics of the device. Specifically, the evacuation apparatus can be selected from a sorption pump, an ion pump, and so on.

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The partial pressure of the organic component in the evacuation apparatus is set to a partial pressure under which there is little carbon or carbon compound newly deposited, and is preferably not more than 1×10^{-8} Torr and particularly preferably not more than 1×10^{-10} Torr. It is further preferred that the whole of the vacuum apparatus be heated during evacuation of the inside of the vacuum apparatus so as to facilitate removal of molecules of the organic

substance adsorbing to the inner wall of the vacuum apparatus and to the electron-emitting device. The heating condition at this time is desirably the temperature of 150 to 300 °C and the heating time of not less than several hours, but the heating condition is not limited particularly to this condition.

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The ambience during driving after completion of the stabilization step is preferably maintained in the ambience at the end of the above stabilization operation, but it is not limited to this. Sufficient characteristics can be maintained by an ambience from which the organic substance is removed adequately but the vacuum degree of which is a little degraded.

By employing such a vacuum ambience, deposition of new carbon substance can be suppressed, whereby the device current If and emission current Ie are stabilized as a result.

Next described is a second production method where the carbon or diamondlike carbon is formed in liquid. The method will be described as to the case where the device is constructed in the structure of either Fig. 26A or Fig. 26B.

(Step 1) Step of forming the lower electrode of the metal or the semiconductor on the substrate

This step is carried out in the same manner as the method described in step 1 of the first production method.

(Step 2) Step of anodizing the lower electrode

This step is also carried out in the same

manner as the method described in step 2 of the first

production method and, after the anodic oxidation and

widening step, the anodized substrate is washed with

water and is taken into the electrolytic tank of (step

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(Step 3) Step of forming the electron-emitting bodies in the pores of the anodic oxidation layer (under existence of organic material of liquid state)

This step is a step of forming the electronemitting bodies in the pores of the aforementioned anodic oxide layer by applying the voltage to the electrode 53 of Fig. 15 and the lower electrode under existence of an organic material of a liquid state.

Using the apparatus similar to Fig. 15, electrolysis is conducted in the electrolyte solution of alcohol between the cathode of the lower electrode side and the anode, whereby diamondlike carbon can be deposited from the lower electrode side in the pores formed by the anodic oxidation.

The diamondlike carbon grows in the columnar shape in the pores with a lapse of the electrolytic time.

25 (Step 4) Step of forming the upper electrode on the metal or the semiconductor thus anodized

The upper electrode is formed in the thickness

of not more than 20 nm in the same manner as the lower electrode was.

(Step 5) Stabilization step

This step is carried out in the same manner as the stabilization step described in step 5 of the first production method.

[Example 1 of the fourth embodiment]

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The electron-emitting devices were produced in the same structure as in Figs. 7A and 7B. Production steps of the present example will be described specifically.

(Step 1: step of forming the lower electrodes of metal on substrate)

The substrate 1 was prepared by depositing

SiO, in the thickness of 1 µm on soda lime glass and the substrate 1 was washed well with detergent, pure water, and organic solvent or the like. Then the material of Al for the lower electrodes was deposited in the thickness of 500 nm on the substrate by sputtering and thereafter the lower electrode wires 71 were formed in stripes on the substrate 1 by the photolithography technology. For using parts of the lower electrode wires 71 as terminals, they were covered with a known mask resin for plating.

25 (Step 2: step of anodizing the lower electrodes)

Using the apparatus of Fig. 15, the anodic oxidation was carried out to anodize parts of the Al

lower electrodes prepared in (step 1).

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was an aqueous solution of oxalic acid 30 g/l. The electrode 53 was a Pt electrode. The anodic oxidation was carried on at 5 °C for five minutes by the constant voltage of 40 V from the power supply 55 with the cathode of the electrode 53 and the anode of the lower wires 71 provided on the substrate 1. On this occasion, the initial current density was 300 mA/cm², but the current density decreased with progress of the anodic oxidation and thereafter increased once to be saturated. Then the substrate with the anodic oxide layers was immersed in an aqueous solution of phosphoric acid for thirty minutes to remove the dense anodic oxide layer and thereafter washed well with water.

(Step 3: step of forming columnar metal in the pores of the anodic oxide layers)

Formation of the columnar metal in the pores was carried out using the apparatus of Fig. 16. In this step Ni was electrodeposited by the constant current at the current density of 1 mA/cm², using the Pt electrode as the counter electrode 91 and 5 % NiSO₄ and 4 % H₃BO₃ as the electrodeposition solution 94 containing the metal. An electrodeposition amount of columnar Ni was controlled by time and the columnar Ni was formed in each pore. The electrodeposition time

was 100 seconds.

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(Step 4: step of forming the upper electrode on the metal or the semiconductor thus anodized)

The upper electrode 72 was made in the thickness of 10 nm in the same manner as the lower electrodes were.

(Step 5: step of forming carbon in the pores of the anodic oxide layers (under existence of organic material of gas state))

10 The substrate 1 was set in the vacuum chamber also serving as a measuring device and the voltage was applied to the upper electrode and lower electrodes under an ambience containing gas of acetone at 10-1 Pa. In step 3, three devices out of the five devices were 15 processed by applying the rectangular waves of the voltage waveform having the pulse width T1 of 1 ms and the pulse spacing T2 of 10 ms in the pulse waveform of Fig. 6A with the lower electrode side at the higher potential for fifteen minutes. Thereafter, the upper 20 electrode was kept at the higher potential and the voltage was applied for five minutes. At the same time, the current of device was monitored. The voltage was 17 V. The two remaining devices out of the five devices were processed by applying the voltage of 17 V 25 similarly in the pulse waveform of Fig. 6B for twenty minutes.

(Step 6: stabilization step)

Then the acetone gas was exhausted sufficiently and thereafter the system was evacuated for two hours while being heated at 300 °C.

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Then the substrate was set in the vacuum process system of Fig. 5 and the voltage was applied to the lower electrode and upper electrode of each device, and to the anode electrode to measure the currents (the device current and emission current) and the device voltage characteristics. Further, electron beams were observed by luminescence of the fluorescent member placed at the anode. After the measurements, the sample thus formed was then observed with the electron microscope, TEM, and so on.

The device current and emission current both of each device demonstrated the monotonically increasing characteristics over their threshold. The current was negligible below the threshold (called Vth). Values of emission current of the devices obtained with application of the pulses of Fig. 6A were equivalent to those of the devices obtained with application of the pulses of Fig. 6B and, therefore, their emission efficiencies were also equivalent.

In observation with the electron emission, the regular pores were observed in the anodic oxide layers. The density of the pores was 1 \times 10 9 pores/cm 2 .

Further, cross-sectional samples were prepared and the inside of the pores was observed. The cross

sections of the devices were as illustrated in Fig. 29A and Fig. 29B. In Figs. 29A and 29B, the same reference symbols as those in Figs. 26A and 26B denote like portions. Fig. 29A is a cross section of the devices in which carbon was formed by applying the pulses of Fig. 6A in step 5, while Fig. 29B is a cross section of the devices in which carbon was formed by applying the pulses of Fig. 6B in step 5. Numeral 111 represents columnar metal Ni, 112 carbon formed in the columnar shape in the pores, 113 carbon formed on the upper electrode side, and 114 a small gap.

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As illustrated in Fig. 29A, where the carbon was formed with application of the pulses of Fig. 6A, the Ni metal was deposited in the columnar shape 110 nm high in the pores from the lower electrode 2 of Al and columnar amorphous carbon was further formed in the pores on the top surface of columnar Ni. Further, amorphous carbon was also formed similarly on the side of the upper electrode 4. A small gap was formed between the carbon on the upper electrode 4 side and the carbon on the lower electrode 2 side and the gap was formed at the edge of the upper electrode. The gap was several nm. The thickness of the anodic oxide film was 150 nm.

On the other hand, where the carbon was formed with application of the pulses of Fig. 6B, as illustrated in Fig. 29B, the Ni metal was deposited in

the columnar shape in the pores on the lower electrode 2 of Al and columnar amorphous carbon was further formed in the pores on the top surface of columnar Ni. Further, amorphous carbon was also formed similarly on the side of the upper electrode 4. The carbon was formed to the position 20 nm apart from the bottom surface of the upper electrode and a small gap was formed between the two carbon layers. The gap was several nm.

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The above proved the following. First, the metal is anodized, the columnar metal is formed in the pores, and the columnar carbon is formed in the pores on the top surface of the columnar metal. Second, the small gap of several nm is formed between the carbon films on the upper electrode side and on the lower electrode side. Third, the emission current and electron emission efficiency are equivalent as long as the small gap is located in the range of 20 nm from the bottom surface of the upper electrode. Since the distance from the gap to the top surface of the upper electrode is not more than 30 nm including the thickness of the upper electrode in the both examples, the probability is assumed to be low of loss of the electrons emitted from the lower electrode side, in the pores. Fourth, the stabilization step enables the device current and emission current to demonstrate the monotonically increasing characteristics without

occurrence of the voltage-controlled negative resistance characteristics, or the VCNR characteristics.

[Example 2 of the fourth embodiment]

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In the present example the substrate was constructed in the device layout similar to Example 1 of the fourth embodiment. The upper electrode was formed in a variety of thicknesses and influence thereof was investigated. Step 1 to step 3, and step 6 were carried out in the same manner as in Example 1. The description of step 1 to step 3, and step 6 will be omitted herein and only steps 4 and 5 will be described in detail.

(Step 1: step of forming the lower electrodes of metal on the substrate)

This step was carried out in the same manner as step 1 of Example 1.

(Step 2: step of anodizing the lower electrodes)

This step was carried out in the same manner as step 2 of Example 1.

(Step 3: step of forming columnar metal in the pores of the anodic oxide layers)

This step was carried out in the same manner as step 3 of Example 1.

25 (Step 4: step of forming the upper electrode on the metal or the semiconductor thus anodized)

The upper electrode 72 was formed in either of

four thicknesses of 5, 10, 100, and 500 nm on each substrate in the same manner as the lower electrodes, thus forming four substrates.

(Step 5: step of forming carbon in the pores of the anodic oxide layers (under existence of organic material of gas shape))

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also serving as a measuring device and the voltage was applied to the upper electrode and lower electrode under an ambience containing gas of acetone at 10⁻¹ Pa. Three devices out of the five devices were processed by applying the rectangular waves of the voltage waveform having the pulse width Tl of 1 ms and the pulse spacing T2 of 10 ms in the pulse waveform of Fig. 6A for fifteen minutes with the lower electrode side at the higher potential. After that, the upper electrode was kept at the higher potential and the voltage was applied for five minutes. At the same time, the current of device was monitored. The voltage was 17 V. (Step 6: stabilization step)

This step was carried out in the same manner as step 2 of the Example 1.

Next, each substrate was set in the vacuum process system of Fig. 5 and the voltage was applied to the lower electrode and upper electrode of each device, and to the anode electrode to measure the currents (the device current and emission current) and the device

voltage characteristics. Further, the electron beam was observed by luminescence of the fluorescent member placed at the anode.

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Fig. 30 shows the relation between thickness of the upper electrode and electron emission efficiency.

As shown in Fig. 30, the electron emission efficiency did not decrease below the thickness of about 200 nm and then decreased with increasing thickness of the upper electrode over 200 nm. The electron emission efficiency is defined as a ratio of emission current to device current. Further, the beam size also decreased.

In observation of the form of the upper electrode, particularly, in the case of the upper electrode having the large thickness, where the thickness was greater than the diameter of the pores, the inside of the pores was also covered in part. When the small gap was observed with section TEM, the small gap was formed at the edge of the bottom surface of the upper electrode in either sample, as in Example 1.

The above verified the following. First, the small gap is formed at the edge of the upper electrode, irrespective of the thickness of the upper electrode. Second, the emission current and electron emission efficiency decrease, depending upon the thickness of the upper electrode. This is assumed to be due to the high probability of loss at the upper electrode of the porous shape, of the electrons emitted from the lower

electrode side.

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[Example 3 of the fourth embodiment]

In the present example the substrate was constructed in the device layout similar to Example 1 of the fourth embodiment. In the present example, SiO₂ was used as the insulating layer instead of the anodic oxide layer of aluminum in Example 1. Production steps of the present example will be described specifically. (Step 1: step of forming the lower electrodes of metal on the substrate)

The substrate 1 was prepared by depositing SiO₂ in the thickness of 1 μm on soda lime glass and then the substrate 1 was washed well with detergent, pure water, and organic solvent or the like. The material Pt for the lower electrode was deposited in the thickness of 500 nm on the substrate by sputtering and thereafter the lower electrode wires 71 were formed in stripes on the substrate 1 by the photolithography technology.

20 (Step 2: step of forming the insulating layer)

Next, SiO_2 was deposited in the thickness of 50 nm by sputtering.

(Step 3: step of farming the upper electrode on the insulating layer)

The upper electrode 72 was made of Pt in the thickness of 10 nm in the same manner as the lower electrodes were.

(Step 4: step of forming the pores in the insulating layer)

In the stack structure of lower electrode / ${\rm SiO_2}$ / upper electrode as described above, four types of pores were formed as follows by the focused ion beam method; (the diameter 50 nm and the pitch 100 nm of the pores), (the diameter 200 nm and the pitch 400 nm of the pores), (the diameter 500 nm and the pitch 1000 nm of the pores), and (the diameter 1000 nm and the pitch 2000 nm of the pores). Here, the pitch is a distance between centers of adjacent pores.

(Step 5: step of forming carbon in the pores of the insulating layer (under existence of organic material of gas shape))

The substrate 1 was set in the vacuum chamber also serving as a measuring device and the voltage was applied to the upper electrode and lower electrode under an ambience containing gas of acetone at 10⁻² Pa. The rectangular waves of the voltage waveform having the pulse width Tl of 1 ms and the pulse spacing T2 of 10 ms in the pulse waveform of Fig. 6A were applied for fifteen minutes and then the lower electrode side was kept at the higher potential for five minutes.

(Step 6: stabilization step)

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Then the acetone gas was exhausted sufficiently and thereafter the system was evacuated for two hours while being heated at 300 °C.

Then the substrate was set in the vacuum process system of Fig. 5 and the voltage was applied to the lower electrode and upper electrode of each device, and to the anode electrode to measure the currents (the device current and emission current), and the device voltage characteristics.

The electron emission efficiency was dependent upon the diameter of the pores as illustrated in Fig. 31, and the electron emission efficiency increased with decreasing diameter of pore.

[Example 4 of the fourth embodiment]

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The present example is an example of application to the image pickup device of Figs. 9A and 9B described previously, in which a plurality of electron-emitting devices prepared by the same method as in Example 1 of the fourth embodiment are placed in a two-dimensional array on the substrate.

The production method of the image pickup device of the present example is the same as in the first embodiment. The image pickup device produced in this way was operated based on the principle of operation stated previously, whereupon the signal current was obtained in 1:1 correspondence to the size of the electron-emitting device, thereby verifying the operation.

[Example 5 of the fourth embodiment]

The present example is an example of

construction of the display device of Figs. 10A and 10B described previously, in which a plurality of electron-emitting devices produced by the same method as in Example 1 of the fourth embodiment are arrayed in a two-dimensional pattern on the substrate. The production method of the display device of the present example is the same as in the first embodiment. The display device produced in this way was operated based on the principle of operation discussed previously, and a bright image was displayed in high definition.

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According to the present invention in the first embodiment as described above, the electron-emitting device is constructed in such structure that the insulating layer having the pores formed by anodic oxidation or the like is provided on the lower electrode, at least carbon is formed in the pores, and the gap is given between the carbon and the upper electrode; therefore, when the voltage is applied between the lower electrode and the upper electrode so as to establish the higher potential on the upper electrode, the electrons injected from the lower electrode tunnel into the vacuum to be emitted. Since the distance of the gap between the carbon formed from the lower electrode, and the upper electrode is nearly constant, the characteristics of the electron-emitting device with little variation can be obtained without dependence of the driving voltage on the thickness of

the insulating layer, different from the conventional MIM electron-emitting devices. Since the electronemitting bodies grown from the lower electrode side is of at least one of graphite, amorphous carbon, and 5 diamondlike carbon, the device is produced with excellent heat resistance and with stable electron emission characteristics in good repeatability. Since the pores are formed in high density and further on the regular basis, the electron-emitting device can be 10 obtained with large emission current and with high The spread of the electron beam is efficiency. decreased and the electron beam equivalent to the formation region of electron emitting device can be formed depending upon conditioning. When an electron 15 source is constructed by placing a plurality of such electron-emitting devices of the present invention, the stable electron source can be provided with little variation from the above reasons. When the electron source is constructed in such structure that the 20 plurality of electron-emitting devices thus placed are located at intersecting portions between the upper wires electrically connected to the upper electrodes and the lower wires electrically connected to the lower electrodes and that the upper wires and the lower wires are arranged nearly perpendicular to each other, a specific electron-emitting device can be selected and modulated out of the plurality of electron-emitting

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devices, by the voltage applied to an upper wire and a lower wire thereof. An image pickup device with high resolution and with excellent uniformity can be provided with little variation by combining the above electron source with a photoconductive member disposed opposite to the electron source. Further, a display device with high definition and with excellent uniformity can be provided with little variation by combining the above electron source of the present invention with an image forming member disposed opposite to the electron source.

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According to the present invention in the second embodiment, the electron-emitting device is constructed in such structure that on the substrate there are the lower electrode, the insulating layer having the pores, and the upper electrode stacked in this order, the insulating layer has the pores, and the electron-emitting regions are provided in the pores, wherein each electron-emitting region is comprised of the small gaps between the lower electrode and the upper electrode and wherein each small gap is formed by the conductive body formed along the inner wall of pore and the upper electrode; therefore, when the voltage is applied between the lower electrode and the upper electrode so as to place the higher potential on the upper electrode, the electrons from the lower electrode tunnel through the gap between the lower electrode and

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the upper electrode into the vacuum and the electrons are efficiently emitted with being affected by the potential of the conductive body formed along the inner wall of pore. In addition, because the distance from the small gap to the top surface of the upper electrode is not more than 200 nm, the electrons colliding with and scattered by the upper electrode do not undergo repetitive scattering, thereby increasing the electron emission efficiency. Since the length of the pores is not more than 500 nm, the singular point of the electric field is constricted even by the potential of the upper electrode of the lower voltage, thereby increasing the electron emission efficiency. Since the distance of the gap between the conductive body formed along the inner wall of pore on the lower electrode, and the upper electrode is determined by the carbon material formed and the voltage applied and is almost constant, the characteristics of the electron-emitting device with little variation can be obtained without dependence of the driving voltage on the thickness of the insulating layer, unlike the conventional MIM electron-emitting devices. Since the electron-emitting bodies of the conductive material grown from the lower electrode side are of at least either one of graphite, amorphous carbon, and diamondlike carbon, the device can be produced with excellent heat resistance and with stable electron emission characteristics in good

repeatability. The conductive bodies may be constructed in such structure that a conductive body of columnar metal or the like is preliminarily formed in each pore and rim-shape carbon is further formed along 5 the inner wall of pore on the columnar metal. In this case, the insulating layer can be made thicker, and the capacitance is thus lowered of the insulating layer between the upper electrode and the lower electrode, which is advantageous in driving of the electron-10 emitting device. Since the pores can be formed in high density and on the regular basis, the efficient electron-emitting device can be obtained with large emission current. Since emission of electrons from the conductive electron-emitting bodies formed in the pores 15 mainly occurs from the linear electron-emitting bodies of the rim shape, the electron-emitting region can be increased drastically, as compared with the small region at the cone tip in the conventional field emission devices. While the conventional surface 20 conduction electron-emitting devices have the onedimensional or linear electron-emitting region, the electron-emitting region of the present invention can be formed two-dimensionally and can thus be increased drastically. Accordingly, the emission current density 25 (a ratio of emission current to electron emission area) is decreased, whereby degradation can be suppressed of the characteristics of the electron-emitting device.

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When compared with the conventional field emission devices, the spread of electron beam is decreased and the electron beam equivalent to the formation region of the electron-emitting device can be formed depending upon the conditions. When an electron source is constructed by arraying a plurality of such electronemitting devices of the present invention, the stable electron source can be provided with little variation from the above reasons. When the electron source is constructed in such structure that the plurality of electron-emitting devices thus arranged are located at intersecting points between the upper wires electrically connected to the upper electrodes and the lower wires electrically connected to the lower electrodes or that each device is located near each intersecting point and the upper wires and the lower wires are arranged nearly perpendicular to each other, a specific electron-emitting device can be selected and modulated out of the plurality of electron-emitting devices, by the voltage applied to an upper wire and a lower wire thereof. When the electron-emitting devices are not located at the intersecting points between the upper wires and the lower wires, but are located near the intersecting points, degrees of freedom are increased for design of wires and devices. Namely, the size of device can be selected so as to match with a necessary emitted electron amount. The degrees of

freedom of design are also increased, because the decrease of the capacitance at the intersecting point between wires separates the size from the device size designed from the necessary electron emission amount of device. An image pickup device with high resolution and with excellent uniformity can be provided with little variation by combining the above electron source with a photoconductive member disposed opposite to the electron source. Further, an image forming apparatus with high definition and with excellent uniformity can be provided with little variation by combining the above electron source of the present invention with an image forming member disposed opposite to the electron source.

According to the present invention in the third embodiment, the electron-emitting device is constructed in such structure that on the substrate there are the lower electrode, the insulating layer having the pores, and the upper electrode stacked in this order, the insulating layer has the pores, and the electron-emitting bodies are provided in the pores, wherein, with the thickness t of the upper electrode, the length L of the pores, and the mean free path λ of electron transmission of the upper electrode, the device satisfies the condition of $0.5 \times L \le t < 2\lambda$; therefore, when the voltage is applied between the lower electrode and the upper electrode so as to establish the higher

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potential on the upper electrode, the electrons injected from the lower electrode tunnel from the electron-emitting bodies into the vacuum, further pass through the upper electrode, and fly to the anode plate. Since the thickness of the upper electrode is not less than 0.5 x L where L is the length of the pores, the upper electrode can cover the apertures of the pores. Since the thickness of the upper electrode is not more than 2λ where λ is the mean free path of electron transmission of the upper electrode, the emitted electrons can efficiently pass through the upper electrode to reach the anode plate. Since the space between the electron-emitting bodies and the upper electrode is the vacuum with small dielectric constant, scattering of electron due to the insulating layer does not occur, when compared with the MIM type provided with the insulating layer, and loss of emitted electrons is thus decreased. Further, the electric capacitance is lowered considerably, which is advantageous in driving of the electron-emitting device, e.g., in power consumption. Since the electron-transmitting portions of the upper electrode have the large mean free path of electron transmission and are of the carbon material having at least either one of graphite, amorphous carbon, and diamondlike carbon with excellent electron transmittance, the emitted electrons efficiently pass through the upper

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electrode to reach the anode electrode. Since carbon is a material with high heat resistance, there occurs little degradation during driving of the electronemitting device, whereby stability is enhanced. Since the carbon material is bound by covalent bond, the shape of the upper electrode covering the regions above the pores can be implemented easier than the metal electrode. In the case of the electron-emitting device of the present invention where the electron-emitting bodies are the needlelike electrodes deposited on the lower electrode or the small particles deposited on the lower electrode, the local electric field is large and the driving voltage is decreased because of the pores, thereby lowering power consumption. In the case of the electron-emitting device of the present invention where the electron-emitting bodies are the rim-shape conductive bodies formed along the inner walls of the pores or the columnar conductive bodies formed in the pores and where there is the small gap between the electron-emitting bodies and the upper electrode, the driving voltage is low because of the small gap and the capacitance is lowered because of the vacuum. Further, where the conductive bodies of the columnar shape are provided between the electron-emitting bodies and the lower electrode, the thickness of the insulating layer can be separated from the electron emission field and the thickness of the insulating layer can thus be made

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larger. This can decrease the capacitance between the upper electrode and the lower electrode, which is advantageous in driving. Since the pores can be formed in high density and on the regular basis, the efficient electron-emitting device can be obtained with large emission current. Since the device is driven at the low emission current density (the ratio of emission current to electron emission area) in practical driving, degradation of the characteristics of the electron-emitting device can be suppressed. When the electron-emitting device of the present invention is compared with the conventional field emission devices having the apertures in the upper electrode above the pores, the device of the invention has the upper electrode above the pores as well; therefore, the spread of electron beam is decreased and the electron beam equivalent to that by the MIM device can be formed. When an electron source is constructed by arraying a plurality of such electron-emitting devices of the present invention, the stable electron source can be provided with high definition from the above reasons. When the electron source is constructed in such structure that the plurality of electron-emitting devices thus arranged are located at intersecting points between the upper wires electrically connected to the upper electrodes and the lower wires electrically connected to the lower electrodes or that

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each device is located near each intersecting point and the upper wires and the lower wires are arranged nearly perpendicular to each other, a specific electronemitting device can be selected and modulated out of the plurality of electron-emitting devices, by the voltage applied to an upper wire and a lower wire thereof. When the electron-emitting devices are not located at the intersecting points between the upper wires and the lower wires, but are located near the intersecting points, degrees of freedom are increased for design of wires and devices. Namely, the size of device can be selected so as to match with a necessary emitted electron amount. The degrees of freedom of design are also increased, because the decrease of the capacitance at the intersecting point between wires separates the size from the device size designed from the necessary electron emission amount of device. image pickup device with high resolution and with excellent uniformity can be provided with little variation by combining the above electron source with a photoconductive member disposed opposite to the electron source. Further, an image forming apparatus with high definition and with excellent uniformity can be provided with little variation by combining the above electron source of the present invention with an image forming member disposed opposite to the electron source.

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According to the present invention in the fourth embodiment, the electron-emitting device is constructed in such structure that on the substrate there are the lower electrode, the insulating layer having the pores, and the upper electrode stacked in this order, the insulating layer has the pores, and the electron-emitting regions are provided in the pores, wherein each electron-emitting regions is comprised of the small gap between the lower electrode and upper electrode and wherein the distance from the small gap to the top surface of the upper electrode is not more than 200 nm; therefore, when the voltage is applied between the lower electrode and the upper electrode so as to establish the higher potential on the upper electrode, the electrons injected from the lower electrode tunnel through the gap between the lower electrode and the upper electrode into the vacuum to be emitted. Further, the electrons colliding with and scattered by the upper electrode do not undergo repetitive scattering, thereby increasing the electron emission efficiency. Since the length of the pores is not more than 500 nm, the singular point of the electric field is constricted even by the potential of the upper electrode of the lower voltage, thereby increasing the electron emission efficiency. Since the distance of the gap between the conductive bodies formed on the lower electrode, and the upper electrode

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is determined by the carbon material formed and the voltage applied and is almost constant, the characteristics of the electron-emitting device with little variation can be obtained without dependence of the driving voltage on the thickness of the insulating layer, unlike the conventional MIM type electronemitting devices. Since the electron-emitting bodies of the conductive bodies of the columnar shape grown from the lower electrode are of at least either one of graphite, amorphous carbon, and diamondlike carbon, the device can be produced with excellent heat resistance and with stable electron emission characteristics in high repeatability. The conductive bodies may be of a stack of the columnar metal and carbon in which the metal is preliminarily formed in the pores and then carbon is formed. In this case, the insulating layer can be made thicker, so that the capacitance is lowered of the insulating layer between the upper electrode and the lower electrode, which is advantageous in driving of the electron-emitting device. Since the pores can be formed in high density and on the regular basis, the efficient electron-emitting device can be obtained with large emission current. Since the electrons from the electron-emitting bodies formed in the pores are emitted mainly from the periphery of the electronemitting bodies of the columnar shape, the electronemitting region can be increased drastically, as

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compared with the small region at the cone tip in the conventional field emission devices. As compared with the conventional surface conduction electron-emitting devices, the electron-emitting region can be increased largely, because it can be formed two-dimensionally. Accordingly, the emission current density (the ratio of emission current to electron emission area) is decreased, so that degradation of the characteristics of the electron-emitting device can be suppressed. the electron-emitting device of the present invention the spread of electron beam is decreased, as compared with the conventional field emission devices. When an electron source is constructed by arraying a plurality of such electron-emitting devices of the present invention, the stable electron source can be provided with little variation from the above reasons. When the electron source is constructed in such structure that the plurality of electron-emitting devices thus arranged are located at intersecting points between the upper wires electrically connected to the upper electrodes and the lower wires electrically connected to the lower electrodes or that each device is located near each intersecting point and the upper wires and the lower wires are arranged nearly perpendicular to each other, a specific electron-emitting device can be selected and modulated out of the plurality of electron-emitting devices, by the voltage applied to an

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upper wire and a lower wire thereof. When the electron-emitting devices are not located at the intersecting points between the upper wires and the lower wires, but are located near the intersecting points, degrees of freedom are increased for design of wires and devices. Namely, the size of device can be selected so as to match with a necessary emitted electron amount. The degrees of freedom of design are also increased, because the decrease of the capacitance at the intersecting point between wires separates the size from the device size designed from the necessary electron emission amount of device. An image pickup device with high resolution and with excellent uniformity can be provided with little variation by combining the above electron source with a photoconductive member disposed opposite to the electron source. Further, an image forming apparatus with high definition and with excellent uniformity can be provided with little variation by combining the above electron source of the present invention with an image forming member disposed opposite to the electron source.

WHAT IS CLAIMED IS:

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 An electron-emitting device comprising a lower electrode, an insulating layer having a pore, and an upper electrode stacked in this order on a substrate,

wherein a carbon deposit is provided in said pore, and a small gap is provided between said upper electrode and said carbon deposit.

- 2. The electron-emitting device according to Claim 1, wherein said insulating layer is an anodic oxide layer.
- 3. The electron-emitting device according to 15 Claim 1, wherein said carbon deposit is electrically conductive and is electrically connected to said lower electrode.
- 4. The electron-emitting device according to

 Claim 1, wherein said carbon deposit is electrically conductive and an insulator is interposed between said lower electrode and said carbon deposit.
- 5. The electron-emitting device according to Claim 1, wherein said carbon deposit is of a polelike shape.

6. The electron-emitting device according to Claim 1, wherein said upper electrode exists in a region except for a region above the pore of an anodic oxide layer.

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7. The electron-emitting device according to Claim 1, wherein said carbon deposit is electrically conductive and is electrically connected to said upper electrode.

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8. The electron-emitting device according to Claim 7, wherein a gap is provided between the carbon deposit on said lower electrode and the carbon deposit connected to said upper electrode.

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9. An electron-emitting device comprising a lower electrode, an insulating layer having a pore, and an upper electrode stacked in this order on a substrate,

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wherein an electron-emitting region is provided in said pore, said electron-emitting region being comprised of a small gap between said lower electrode and upper electrode, said small gap being formed by an electroconductive body of a rim shape formed along an inner wall of said pore, and the upper electrode.

10. The electron-emitting device according to

Claim 9, wherein said insulating layer is an anodic oxide layer.

- 11. The electron-emitting device according to
 5 Claim 9, wherein said electroconductive body formed
 along the inner wall of the pore is formed on an
 electroconductive body of a polelike shape formed in
 said pore.
- 12. The electron-emitting device according to Claim 9, wherein said electroconductive body formed along the inner wall of the pore is a carbon deposit.
- 13. The electron-emitting device according to
 Claim 11, wherein said electroconductive body of the polelike shape is metal.
 - 14. The electron-emitting device according to Claim 9, wherein a distance from said small gap to a top surface of the upper electrode is not more than 200 nm.

- 15. The electron-emitting device according to Claim 9, wherein a length of said pore is not more than 500 nm.
 - 16. The electron-emitting device according to

Claim 9, wherein said small gap is not more than 20 nm.

17. An electron-emitting device comprising a lower electrode, an insulating layer having a pore, and an upper electrode stacked in this order on a substrate,

wherein an electron-emitting body is provided in said pore, and wherein the following condition is satisfied:

10 $0.5 \times L \le t < 2\lambda$

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where t is a thickness of said upper electrode, L is a length of said pore, and λ is a mean free path of electron transmission of said upper electrode.

- 18. The electron-emitting device according to Claim 17, wherein said upper electrode has a carbon deposit.
- 19. The electron-emitting device according to
 20 Claim 17, wherein said electron-emitting body is a needlelike electrode deposited on said lower electrode.
 - 20. The electron-emitting device according to Claim 17, wherein said electron-emitting body is a small particle deposited on said lower electrode.
 - 21. The electron-emitting device according to

Claim 17, wherein said electron-emitting body is an electroconductive body of a rim shape formed along an inner wall of said pore and a small gap is provided between the electroconductive body of the rim shape formed along the inner wall of the pore, and the upper electrode.

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- 22. The electron-emitting device according to Claim 17, wherein said electron-emitting body is an electroconductive body of a columnar shape formed in said pore and a small gap is provided between the electroconductive body of the columnar shape formed in said pore, and the upper electrode.
- 23. The electron-emitting device according to Claim 17, wherein said electron-emitting body is formed on an electroconductive body of a polelike shape formed in said pore.
- 24. The electron-emitting device according to Claim 17, wherein said electron-emitting body has a carbon deposit.
- 25. The electron-emitting device according to Claim 23, wherein said electroconductive body of the polelike shape is metal.

- 26. The electron-emitting device according to Claim 17, wherein said insulating layer is an anodic oxide layer.
- 5 27. The electron-emitting device according to Claim 17, wherein said electron-emitting body lies on an insulating layer formed on the lower electrode.
- 28. An electron-emitting device comprising a lower electrode, an insulating layer having a pore, and an upper electrode stacked in this order on a substrate, wherein an electron-emitting region is provided in said pore,

said electron-emitting region being comprised of a small gap between said lower electrode and upper electrode, and wherein a distance from the small gap to a top surface of the upper electrode is not more than 200 nm.

- 29. The electron-emitting device according to Claim 28, wherein a length of said pore is not more than 500 nm.
- 30. The electron-emitting device according to Claim 28, wherein said small gap is not more than 20 nm.

31. The electron-emitting device according to Claim 28, wherein said small gap is formed by an electroconductive body of a polelike shape formed in said pore, and the upper electrode.

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- 32. The electron-emitting device according to Claim 28, wherein said electroconductive body of the polelike shape is a carbon deposit.
- 10 33. The electron-emitting device according to Claim 28, wherein said electroconductive body of the polelike shape is metal and carbon.
- 34. The electron-emitting device according to
 15 Claim 28, wherein said insulating layer is an anodic
 oxide layer.
 - 35. The electron-emitting device according to Claim 28, wherein said electroconductive body lies on an insulating layer formed on the lower electrode.
 - 36. The electron-emitting device according to Claim 1, wherein said pore is of a cylindrical shape having a side face parallel to a direction of emission of electron.
 - 37. The electron-emitting device according to

Claim 9, wherein said pore is of a cylindrical shape having a side face parallel to a direction of emission of electron.

- 5 38. The electron-emitting device according to Claim 17, wherein said pore is of a cylindrical shape having a side face parallel to a direction of emission of electron.
- 39. The electron-emitting device according to Claim 28, wherein said pore is of a cylindrical shape having a side face parallel to a direction of emission of electron.
- 15 40. The electron-emitting device according to Claim 1, wherein said carbon deposit is at least one of graphite, amorphous carbon, and diamondlike carbon.
- 41. The electron-emitting device according to

 Claim 9, wherein said carbon deposit is at least one of
 graphite, amorphous carbon, and diamondlike carbon.
 - 42. The electron-emitting device according to Claim 17, wherein said carbon deposit is at least one of graphite, amorphous carbon, and diamondlike carbon.

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43. The electron-emitting device according to

Claim 28, wherein said carbon deposit is at least one of graphite, amorphous carbon, and diamondlike carbon.

- 44. An electron source comprising a pluralityof electron-emitting devices as set forth in Claim 1.
 - 45. An electron source comprising a plurality of electron-emitting devices as set forth in Claim 9.
- 10 46. An electron source comprising a plurality of electron-emitting devices as set forth in Claim 17.
 - 47. An electron source comprising a plurality of electron-emitting devices as set forth in Claim 28.

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- 48. The electron source according to Claim 44, wherein said plurality of electron-emitting devices are located at intersecting points between upper wires electrically connected to upper electrodes and lower wires electrically connected to lower electrodes and wherein said upper wires and said lower wires are arranged perpendicular to each other.
- 49. The electron source according to Claim 45,
 wherein said plurality of electron-emitting devices are
 located at intersecting points between upper wires
 electrically connected to upper electrodes and lower

wires electrically connected to lower electrodes and wherein said upper wires and said lower wires are arranged perpendicular to each other.

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50. The electron source according to Claim 46, wherein said plurality of electron-emitting devices are located at intersecting points between upper wires electrically connected to upper electrodes and lower wires electrically connected to lower electrodes and wherein said upper wires and said lower wires are arranged perpendicular to each other.

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51. The electron source according to Claim 47, wherein said plurality of electron-emitting devices are located at intersecting points between upper wires electrically connected to upper electrodes and lower wires electrically connected to lower electrodes and wherein said upper wires and said lower wires are arranged perpendicular to each other.

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52. An image pickup device comprising the electron source as set forth in Claim 44, and a photoconductive member disposed opposite to said electron source.

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53. An image pickup device comprising the electron source as set forth in Claim 45, and a

photoconductive member disposed opposite to said electron source.

54. An image pickup device comprising the electron source as set forth in Claim 46, and a photoconductive member disposed opposite to said electron source.

- 55. An image pickup device comprising the electron source as set forth in Claim 47, and a photoconductive member disposed opposite to said electron source.
- 56. An image pickup device comprising the electron source as set forth in Claim 48, and a photoconductive member disposed opposite to said electron source.
- 57. An image pickup device comprising the electron source as set forth in Claim 49, and a photoconductive member disposed opposite to said electron source.
- 58. An image pickup device comprising the electron source as set forth in Claim 50, and a photoconductive member disposed opposite to said electron source.

59. An image pickup device comprising the electron source as set forth in Claim 51, and a photoconductive member disposed opposite to said electron source.

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- 60. A display device comprising the electron source as set forth in Claim 44, and an image forming member disposed opposite to said electron source.
- 10 61. A display device comprising the electron source as set forth in Claim 45, and an image forming member disposed opposite to said electron source.
 - 62. A display device comprising the electron source as set forth in Claim 46, and an image forming member disposed opposite to said electron source.
 - 63. A display device comprising the electron source as set forth in Claim 47, and an image forming member disposed opposite to said electron source.
 - 64. A display device comprising the electron source as set forth in Claim 48, and an image forming member disposed opposite to said electron source.

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65. A display device comprising the electron source as set forth in Claim 49, and an image forming

member disposed opposite to said electron source.

- 66. A display device comprising the electron source as set forth in Claim 50, and an image forming member disposed opposite to said electron source.
- 67. A display device comprising the electron source as set forth in Claim 51, and an image forming member disposed opposite to said electron source.

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68. A method for producing an electronemitting device comprising a lower electrode, an
insulating layer having a pore, and an upper electrode
stacked in this order on a substrate, said electronemitting device having a carbon deposit in said pore,

said method comprising:

- a step of forming said lower electrode of a metal or a semiconductor on said substrate;
- a step of forming an anodic oxide layer on a surface of said lower electrode;
- a step of producing said carbon deposit in the pore of said anodic oxide layer by applying a voltage under existence of an organic material; and
 - a step of forming the upper electrode.

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69. The method for producing the electronemitting device according to Claim 68, wherein said organic material is a liquid.

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70. A method for producing an electronemitting device comprising a lower electrode, an
insulating layer having a pore, and an upper electrode
stacked in this order on a substrate, said electronemitting device having a carbon deposit in said pore,

said method comprising:

a step of forming said lower electrode of a metal or a semiconductor on said substrate;

a step of forming an anodic oxide layer in a surface of said lower electrode;

a step of forming said upper electrode on said anodic oxide layer in said lower electrode; and

a step of producing a carbon deposit in said pore of said anodic oxide layer by applying a voltage to said upper electrode and said lower electrode, under existence of an organic material.

- 71. The method for producing the electronemitting device according to Claim 70, wherein said organic material is a gas.
- 72. The method for producing the electronemitting device according to Claim 68, wherein said voltage is a pulse-shaped voltage.

- 73. The method for producing the electronemitting device according to Claim 70, wherein said voltage is a pulse-shaped voltage.
- 5 74. The method for producing the electronemitting device according to Claim 68, wherein on the occasion of applying said voltage, said lower electrode is kept at a higher potential.
- 75. The method for producing the electronemitting device according to Claim 70, wherein on the occasion of applying said voltage, said lower electrode is kept at a higher potential.
- 76. The method for producing the electronemitting device according to Claim 68, wherein on the occasion of applying said voltage, a higher potential and a lower potential are alternately applied to said lower electrode.

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- 77. The method for producing the electronemitting device according to Claim 70, wherein on the occasion of applying said voltage, a higher potential and a lower potential are alternately applied to said lower electrode.
 - 78. The method for producing the electron-

emitting device according to Claim 68, wherein said carbon deposit is at least one of graphite, amorphos carbon, and diamondlike carbon.

79. The method for producing the electronemitting device according to Claim 70, wherein said
carbon deposit is at least one of graphite, amorphos
carbon, and diamondlike carbon.

ABSTRACT OF THE DISCLOSURE

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An electron-emitting device disclosed has stable electron emission characteristics with little variation, in high electron emission efficiency, in high definition, and at low driving voltage. The electron-emitting device disclosed is constructed in such structure that on a substrate there are a lower electrode, an insulating layer having pores, and an upper electrode stacked in this order, the insulating layer is an anodic oxide layer, and a carbon deposit is formed in the pores.

FIG. 1A

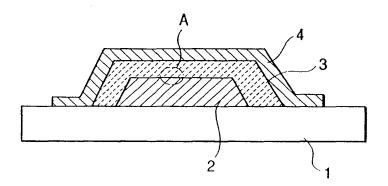
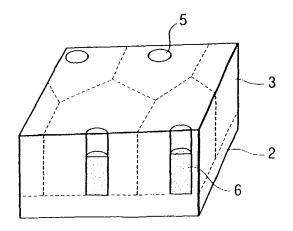


FIG. 1B



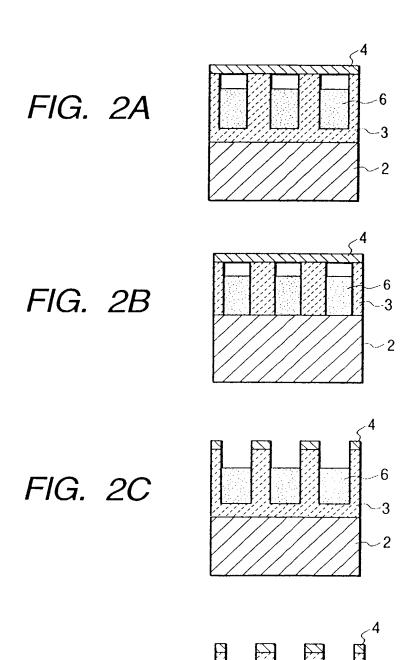


FIG. 2D

FIG. 3

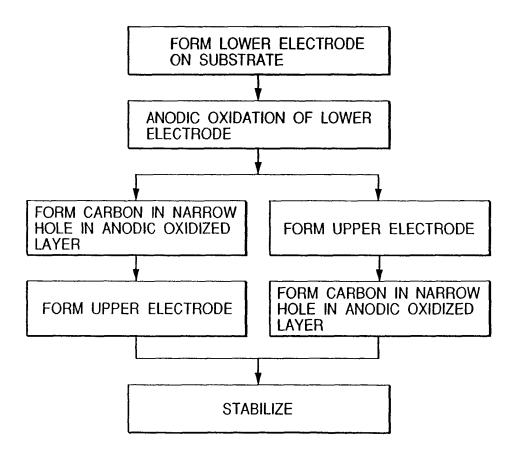
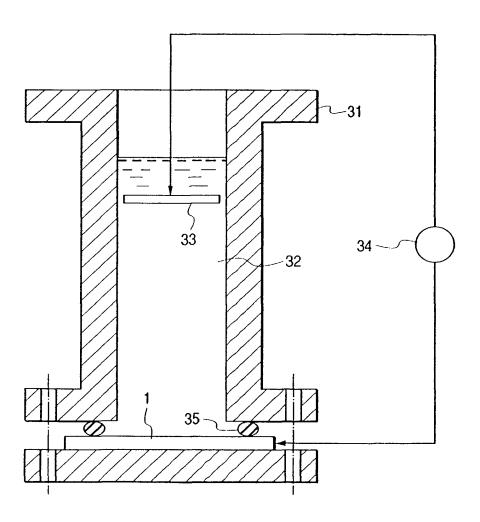


FIG. 4



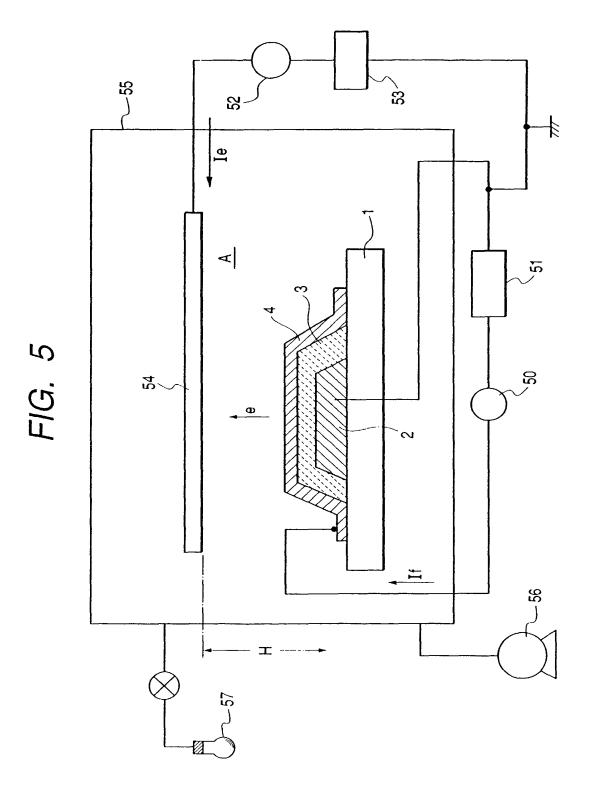


FIG. 6A

PULSE WAVEFORM

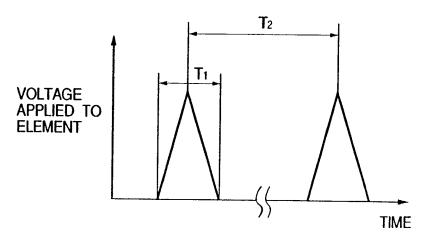


FIG. 6B

PULSE WAVEFORM

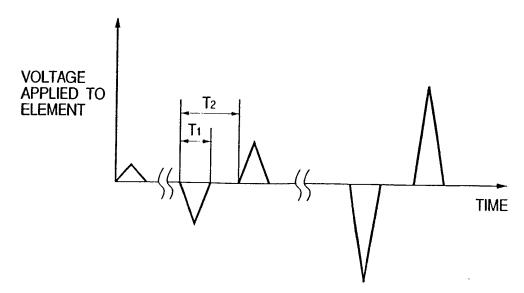


FIG. 7A

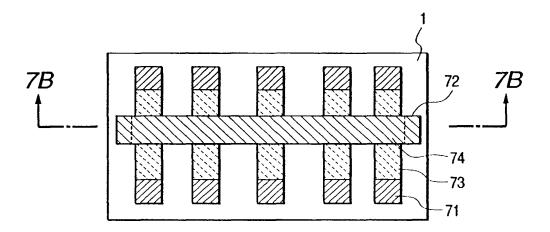


FIG. 7B

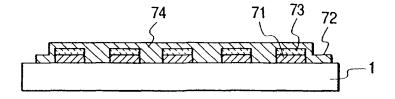


FIG. 8A

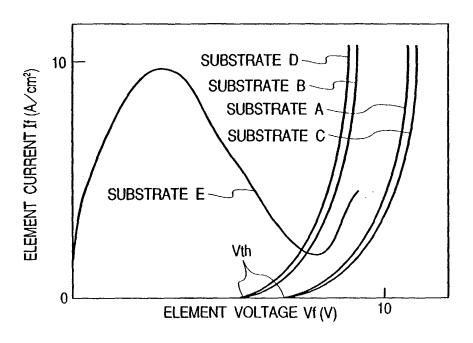


FIG. 8B

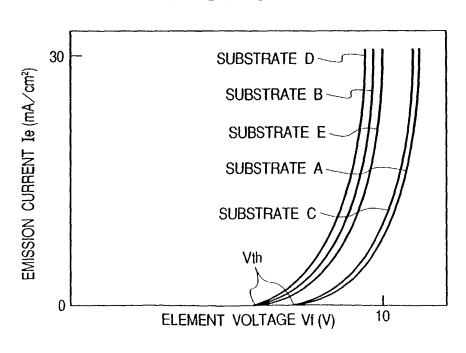


FIG. 9A

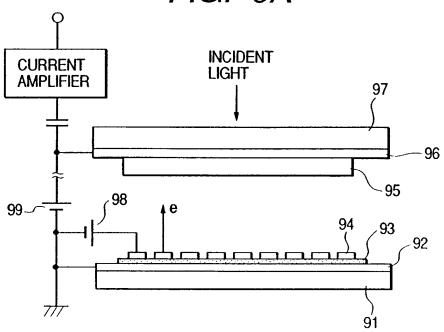


FIG. 9B

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FIG. 10A

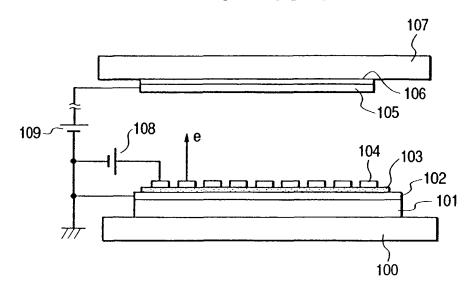


FIG. 10B

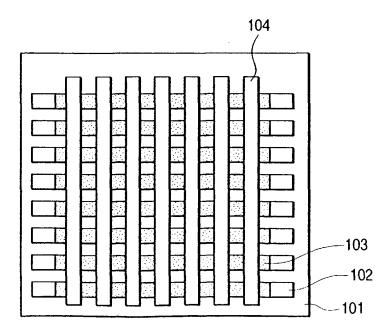


FIG. 11A

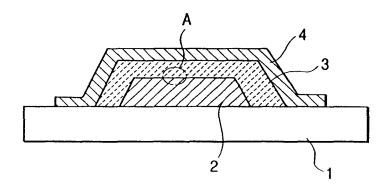
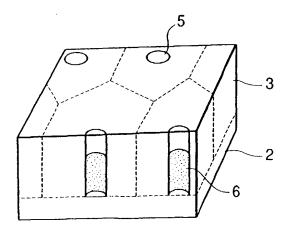


FIG. 11B



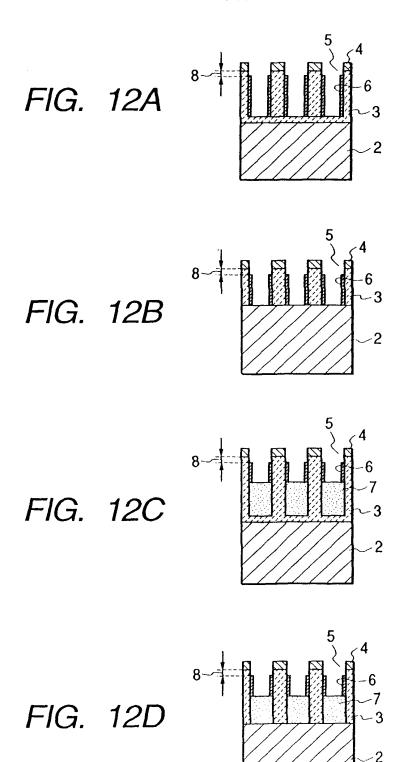
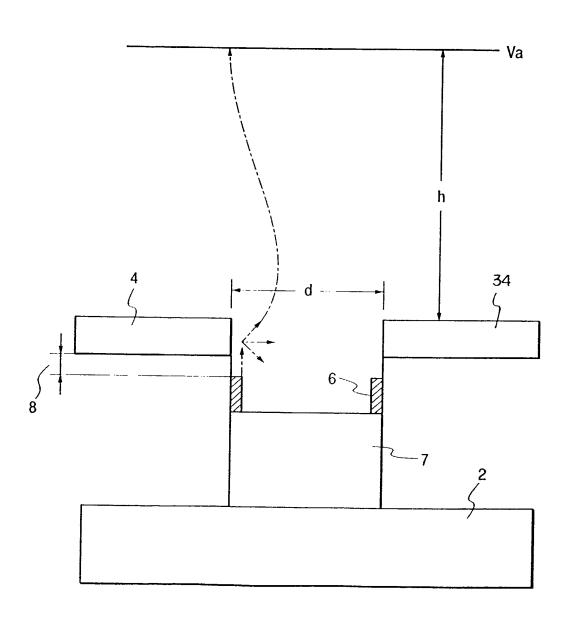


FIG. 13



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FIG. 14

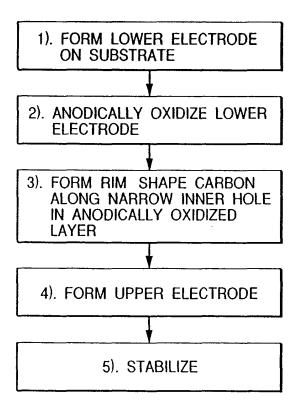


FIG. 15

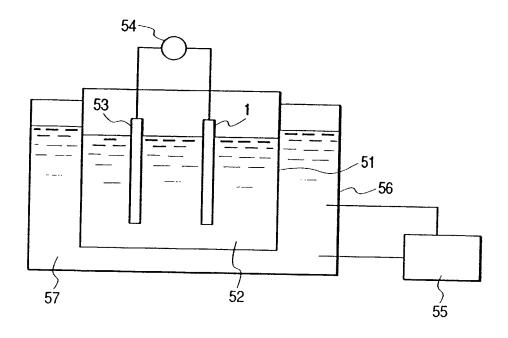


FIG. 16

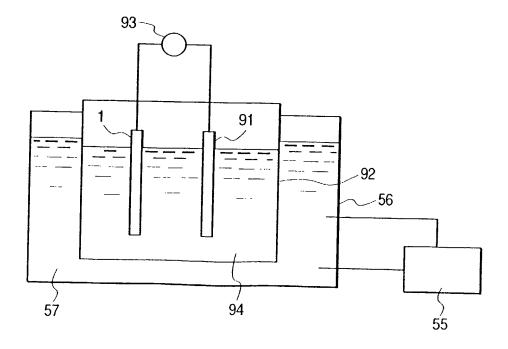


FIG. 17A

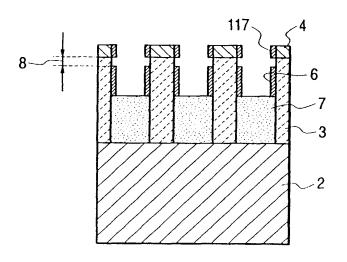


FIG. 17B

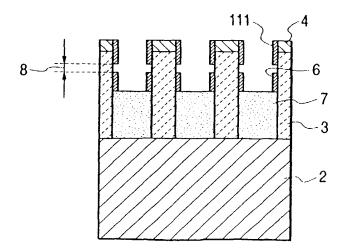


FIG. 18

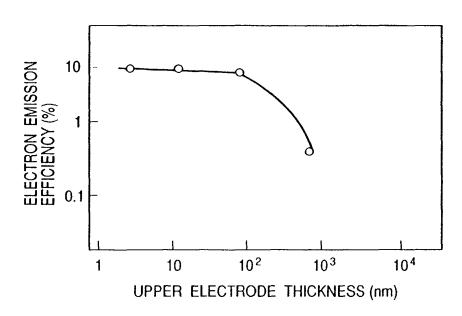


FIG. 19

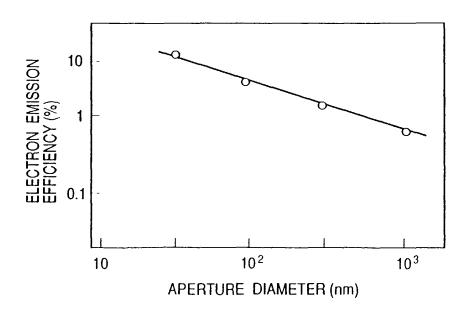


FIG. 20A

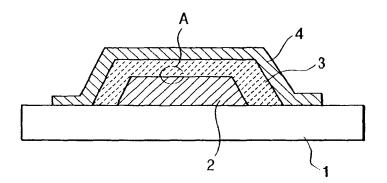


FIG. 20B

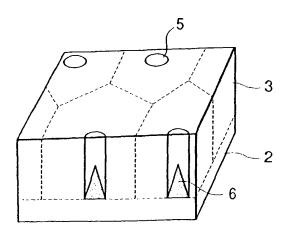


FIG. 21A

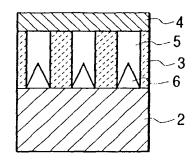


FIG. 21B

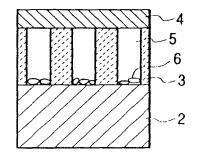


FIG. 21C

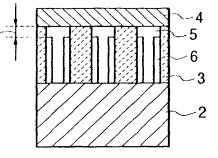


FIG. 21D

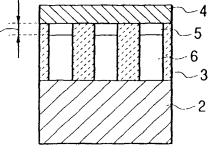


FIG. 22A

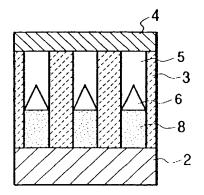


FIG. 22B

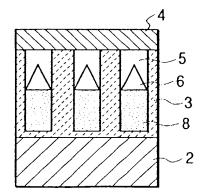


FIG. 23

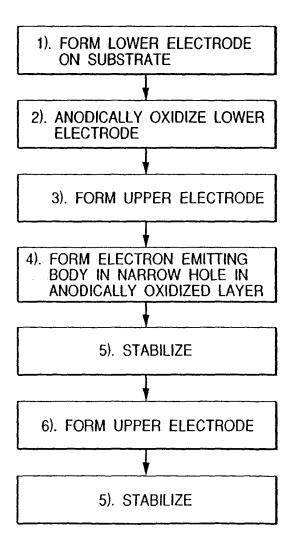


FIG. 24

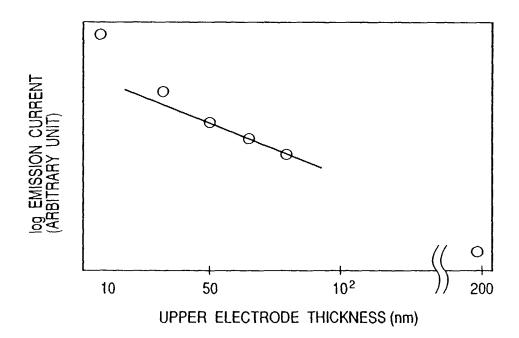


FIG. 25A

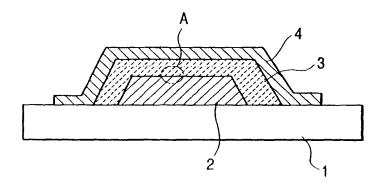


FIG. 25B

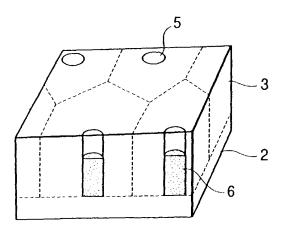


FIG. 26A

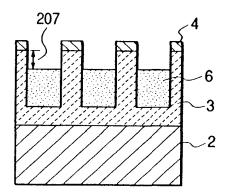


FIG. 26B

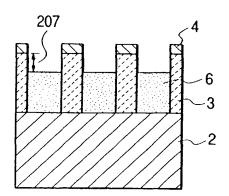


FIG. 27

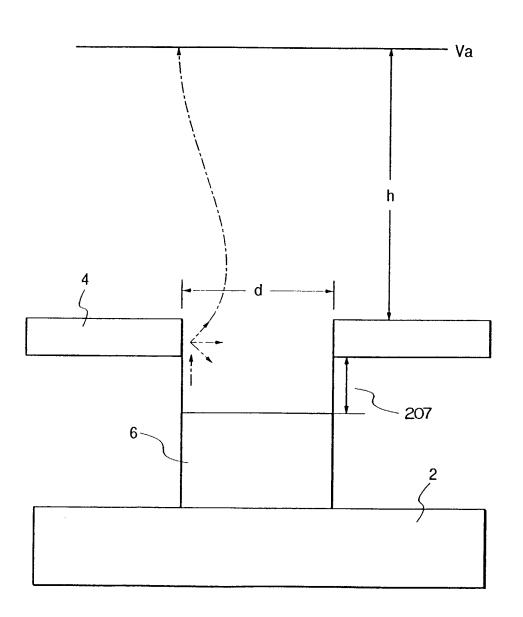


FIG. 28

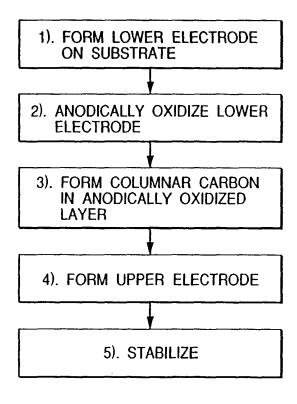


FIG. 29A

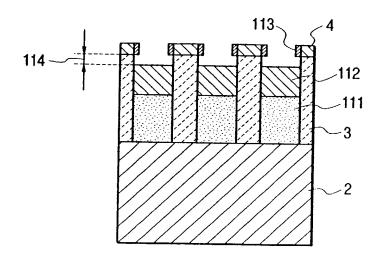


FIG. 29B

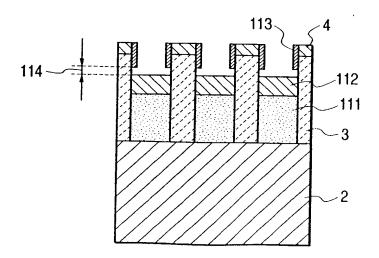


FIG. 30

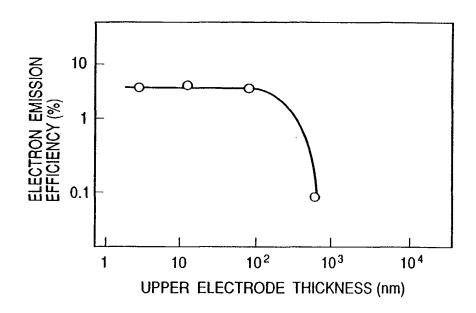


FIG. 31

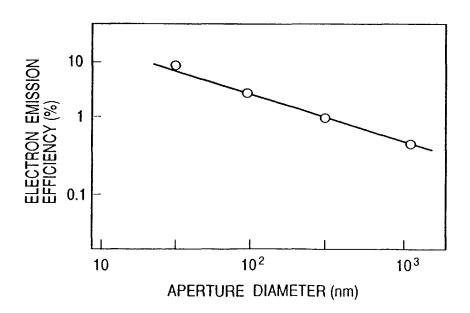


FIG. 32

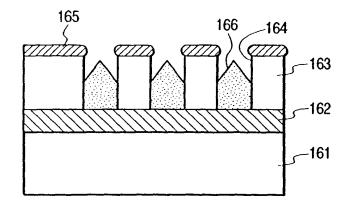


FIG. 33

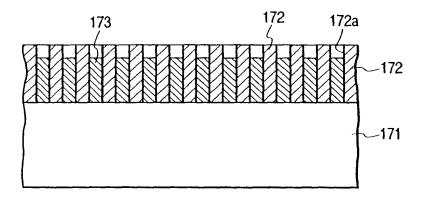


FIG. 34

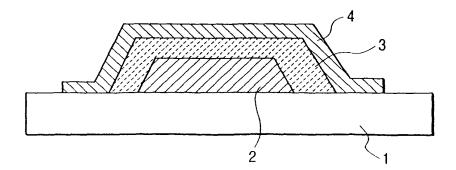


FIG. 35A

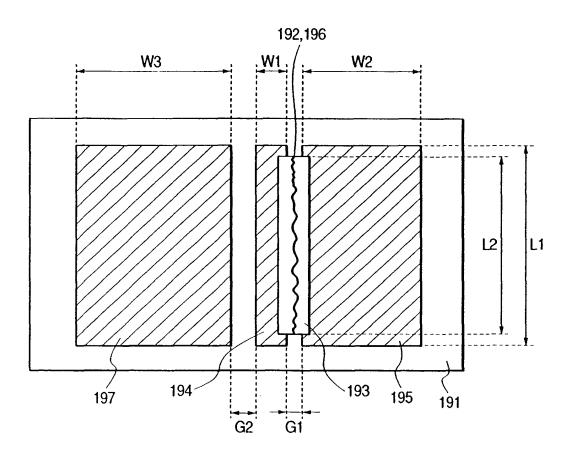
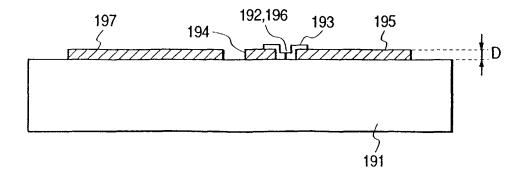


FIG. 35B





CFO 15727 US 09/941,780 D/F . 8-30-01 CAU 2817

ELECTRON-EMITTING DEVICE, ELECTRON-EMITTING APPARATUS,
IMAGE DISPLAY APPARATUS, AND LIGHT-EMITTING APPARATUS

BACKGROUND OF THE INVENTION

5 Field of the Invention

The present invention relates to an electronemitting device, an electron-emitting apparatus, an
electron source and an image-forming apparatus. The
present invention also relates to a display apparatus
such as a television broadcast display, a display for
use in a video conference system or a computer display,
and to an image-forming apparatus designed as an
optical printer using a photosensitive drum or the
like.

15 Related Background Art

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A field emission (FE) type of electron-emitting device which emits electrons from a surface of a metal when a strong electric field of 10^6 V/cm or higher is applied to the metal, and which is one of the known cold cathode electron sources, is attracting attention.

If the FE-type cold electron source is put to practical use, a thin emissive type image display apparatus can be realized. The FE-type cold electron source also contributes to reductions in power consumption and weight of an image display apparatus.

Fig. 13 shows a vertical FE-type cold electron source structure formed of a substrate 131, an emitter

electrode 132, an insulating layer 133, an emitter 135, and an anode 136. The shape of an electron beam with which the anode is irradiated is indicated by 137. This structure is of a Spindt type such that an opening is formed in the insulating layer 133 and the gate electrode 134 provided on the cathode 132, and the emitter 135 having a conical shape is placed in the opening. (This type of structure is disclosed by, for example, C.A. Spindt, "Physical Properties of thin-film field emission cathodes with molybdenum cones", J. Appl. Phys., 47, 5248 (1976).)

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Fig. 14 shows a lateral FE structure formed of a substrate 141, an emitter electrode 142, an insulating layer 143, an emitter 145, and an anode 146. The shape of an electron beam with which the anode is irradiated is indicated by 147. The emitter 145 having an acute extreme end and the gate electrode 144 for drawing out electrons from the extreme end of the emitter are disposed above and parallel to the substrate, and the collector (anode) is formed above the gate electrode and the emitter electrode remote from the substrate (see USP 4,728,851, USP 4,904,895, etc.).

Also, Japanese Patent Application Laid-open No. 8-115652 discloses an electron-emitting device using fibrous carbon which is deposited in a narrow gap by performing thermal cracking of an organic chemical compound gas on a catalyst metal.

In an image display apparatus using one of the above-described FE-type electron sources, an electron beam spot is obtained which has a size (hereinafter referred to as "beam diameter") depending on the distance H between the electron source and the phosphor, the anode voltage Va, and the device drive voltage Vf. The beam diameter is smaller than a millimeter and the image display apparatus has sufficiently high resolution.

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In recent years, however, there has been a tendency to require higher resolution of image display apparatuses.

Further, with the increase in the number of display pixels, power consumption during driving due to the device capacitance of electron-emitting devices is increased. Therefore there is a need to reduce the device capacitance and the drive voltage and to improve the efficiency of electron-emitting devices.

In the above-described Spindt type of electron source, the gate is laminated on the substrate with the insulating layer interposed therebetween, so that parasitic capacitances are produced between large capacitances and a multiplicity of emitters. Moreover, the drive voltage is high, several ten to several hundred volts, and capacitive power consumption is disadvantageously large because of the specific structure.

Also, since the beam of electrons drawn out spreads out, there is a need for a focusing electrode for limiting spreading of the beam. For example, Japanese Patent Application Laid-open No. 7-6714 discloses a method of converging electron trajectories by disposing an electrode for focusing electrons. This method, however, has the problem of an increase in complexity of the manufacturing process, a reduction in electron emission efficiency, etc., due to the addition of the focusing electrode.

In ordinary lateral FE electron sources, electrons emitted from the cathode are liable to impinge on the opposed gate electrode. Therefore the structure of lateral FE electron sources has the problem of a reduction in the efficiency (the ratio of the electron current flowing through the gate and the electron current reaching the anode) and considerable spreading of the beam shape on the anode.

20 SUMMARY OF THE INVENTION

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In view of the above-described problems, an object of the present invention is to provide an electron-emitting device in which the specific capacitance is reduced, which has a lower drive voltage, and which is capable of obtaining a finer electron beam by controlling the trajectory of emitted electrons.

To achieve the above-described object, according

to one aspect of the present invention, there is provided an electron-emitting apparatus comprising:

a first electrode and a second electrode disposed on a surface of a substrate;

first voltage application means for applying to the second electrode a potential higher than a potential applied to the first electrode;

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an electron-emitting member disposed on the first electrode;

a third electrode disposed so as to face the substrate, electrons emitted from the electron-emitting member reaching the third electrode; and

second voltage application means for applying to the third electrode a potential higher than each of the potentials applied to the first and second electrodes, wherein a surface of the electron-emitting member is placed between a plane containing a surface of the second electrode and substantially parallel to the surface of the substrate and a plane containing a surface of the third electrode and substantially parallel to the surface of the substrate. When the distance between the second electrode and the first electrode is d; the potential difference applied between the second electrode and the first electrode by the first voltage application means is V1; the distance between the third electrode and the substrate is H; and the potential difference between the potential applied

to the third electrode by the second voltage application means and the potential applied to the first electrode by the first voltage application means is V2, then an electric field E1 = V1/d is within the range from 1 to 50 times an electric field E2 = V2/H.

According to another aspect of the present invention, there is provided an electron-emitting apparatus comprising:

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a first electrode and a second electrode disposed on a surface of a substrate;

first voltage application means for applying to the second electrode a potential higher than a potential applied to the first electrode;

a plurality of fibers disposed on the first electrode, the fibers containing carbon as a main ingredient;

a third electrode disposed so as to face the substrate, electrons emitted from the fibers reaching the third electrode; and

second voltage application means for applying to
the third electrode a potential higher than each of the
potentials applied to the first and second electrodes,
wherein a surface region of the fibers is placed
between a plane containing a surface of the second
electrode and substantially parallel to the surface of
the substrate and a plane containing a surface of the
third electrode and substantially parallel to the

surface of the substrate.

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In the above-described arrangement, the place at which the electric field concentrates is limited to one side of the region where an emitter material is formed, thereby enabling emitted electrons to be first drawn out toward the extraction electrode (gate electrode) and then made to reach the anode with substantially no possibility of impinging on the extraction electrode. As a result, the electron emission efficiency is improved. Also, there is substantially no possibility of scattering of electrons on the extraction electrode, so that the size of the beam spot obtained on the anode is smaller than that in the conventional device having the problem of scattering on the extraction electrode.

According to still another aspect of the present invention, there is provided an electron-emitting device comprising:

a fiber containing carbon as a main ingredient; and

an electrode for controlling emission of electrodes from the fiber containing carbon as a main ingredient, wherein the fiber containing carbon as a main ingredient has a plurality of layered (laminated) graphenes so as not to be parallel to the axis direction of the fiber.

According to a further aspect of the present invention, there is provided an electron-emitting

device comprising:

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a first electrode and a second electrode disposed on a surface of a substrate, a gap being formed between the first and second electrodes; and

a fiber provided on the first electrode, the fiber containing carbon as a main ingredient, wherein the second electrode comprises an electrode for controlling emission of electrons from the fiber containing carbon as a main ingredient, and wherein the fiber containing carbon as a main ingredient comprises graphene.

The electron-emitting device of the present invention can stably emit electrons in a low vacuum degree at an increased rate for a long time period.

According to the present invention, a lightemitting member is provided on the anode in the
electron-emitting apparatus or above the electronemitting device to form a light-emitting device, an
image display apparatus or the like capable of
operating in a low vacuum degree and effecting highluminance emission/display for a long time period with
stability.

BRIEF DESCRIPTION OF THE DRAWINGS

Figs. 1A and 1B are diagrams showing an example of a basic electron-emitting device in accordance with the present invention;

Figs. 2A and 2B are diagrams showing a second

embodiment of the present invention;

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Figs. 3A and 3B are diagrams showing a third embodiment of the present invention;

Figs. 4A and 4B are diagrams showing a fourth embodiment of the present invention;

Figs. 5A, 5B, 5C, and 5D are diagrams showing fabrication steps in a first embodiment of the present invention;

Fig. 6 is a diagram showing an arrangement for operating the electron-emitting device of the present invention;

Fig. 7 is a diagram showing an operating characteristic of the basic electron-emitting device of the present invention;

15 Fig. 8 is a diagram showing an example of the configuration of a passive matrix circuit using a plurality of electron sources in accordance with the present invention;

Fig. 9 is a diagram showing an example of the construction of an image forming panel using the electron source of the present invention;

Fig. 10 is a diagram showing an example of a circuit for the image forming panel using the electron source of the present invention;

25 Fig. 11 is a diagram schematically showing the structure of a carbon nanotube;

Fig. 12 is a diagram schematically showing the

structure of a graphite nanofiber;

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Fig. 13 is a diagram showing a conventional vertical FE structure; and

Fig. 14 is a diagram showing an example of a conventional lateral FE structure.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Preferred embodiments of the present invention will be described in detail with reference to the accompanying drawings. The description of components of the embodiments made below with respect to the size, material and shape of the components and the relative positions of the components is not intended to limit the scope of the present invention except for particular mention of specified details.

The operating voltage Vf of FE devices is generally determined by the electric field at an extreme end of an emitter obtained from the Poisson equation and by the current density of electron emission current according to the relational expression called "Fowler-Nordheim equation" with a work function of the electric field and the emitter portion used as a parameter.

A stronger electric field is obtained as the electric field necessary for emission of electrons as the distance D between the emitter extreme end and the gate electrode is smaller or the radius r of the

emitter extreme end is smaller.

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On the other hand, the maximum size Xd in the X-direction of the electron beam obtained on the anode (e.g., the maximum reach from the center of the circular beam shape 137 shown in Fig. 13) is expressed in such a form as to be proportional to (Vf/Va) in simple calculation.

As is apparent from this relationship, an increase in Vf results in an increase in beam diameter.

Beam shapes in conventional arrangements will be

Consequently, there is a need to minimize the distance D and the radius of curvature r in order to reduce Vf.

described with reference to Figs. 13 and 14. In Figs. 13 and 14, substrates which are corresponding components of the two arrangements are indicated by 131 and 141; emitter electrodes by 132 and 142; insulating layers by 133 and 143; emitters by 135 and 145; anodes by 136 and 146; the shapes of electron beams with which the anodes are irradiated by 137 and 147.

In the case of the Spindt type described above with reference to Fig. 13, when Vf is applied between the emitter 135 and the gate 134, the strength of the electric field at the extreme end of the projection of the emitter, 135 is increased and electrons are thereby taken out of a conical emitter portion about the extreme end into the vacuum.

The electric field at the extreme end of the emitter is formed based on the shape of the extreme end of the emitter to have a certain finite area on the same, so that electrons are perpendicularly drawn out from the finite emitter extreme end area according to the potential.

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Simultaneously, other electrons are emitted at various angles. Electrons emitted at larger angles are necessarily drawn toward the gate.

As a result, if the gate is formed so as to have a circular opening, the distribution of electrons on the anode 136 shown in Fig. 13 forms a substantially circular beam shape 137. That is, the shape of the beam obtained is closely related to the shape of the drawing gate and to the distance between the gate and the emitter.

In the case of the lateral FE electron source (Fig. 14) in which electrons are drawn out generally along one direction, an extremely strong electric field substantially parallel to the surface of the substrate 141 (lateral electric field) is produced between the emitter 145 and the gate 144, so that part 149 of electrons emitted from the emitter 145 are drawn into the vacuum above the gate 144 while the other electrons are taken into the gate electrode 144.

In the arrangement shown in Fig. 14, electric field vectors toward the anode 146 differ in direction

from those causing emission of electrons (the electric field from the emitter 145 toward the gate 144).

Therefore the distribution of electrons (beam spot) formed by emitted electrons on the anode 146 is increased.

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The electric field of electrons drawn out from the emitter electrode 145 (referred to as "lateral electric field" in the following description for convenience sake while the electric field strengthening effect of the emitter configuration is ignored) and the electric field toward the anode (referred to as "vertical electric field" in the following description) will further be described.

The "lateral electric field" can also be expressed as "electric field in a direction substantially parallel to the surface of substrate 131 (141)" in the arrangement shown in Fig. 13 or 14. It can also be expressed as "electric field in the direction of opposition of gate 144 and emitter 145" with respect to the arrangement shown in Fig. 14 in particular.

Also, the "vertical electric field" can also be expressed as "electric field in a direction substantially perpendicular to the surface of substrate 131 (141)" in the arrangement shown in Fig. 13 or 14, or as "electric field in the direction in which the substrate 131 (141) is opposed to the anode 136 (146)".

In the arrangement shown in Fig. 14, as described

above, electrons emitted from the emitter are first drawn out by the lateral electric field, fly toward the gate, and are then moved upward by the vertical electric field to reach the anode.

Important factors of this effect are the ratio of the strengths of the lateral and vertical electric fields and the relative position of the electron emission point.

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When the lateral electric field is stronger than the vertical electric field by an order of magnitude, the trajectories of almost all of electrons drawn out from the emitter are gradually bent by radial potential produced by the lateral electric field so that the electrons fly toward the gate. A part of the electrons impinging on the gate ejects again in a scattering manner. After ejection, however, the electrons repeat scattering while spreading out along the gate by forming elliptical trajectories again and again and while being reduced in number when ejecting until they are caught by the vertical electric field. Only after the scattered electrons have exceeded an equipotential line formed by the gate potential (which line may be called "stagnation point"), they are moved upward by the vertical electric field.

When the lateral electric field and the vertical electric field are approximately equal in strength, the restraint imposed by the lateral electric field on

electrons drawn out is reduced, although the trajectories of the electrons are bent by the radial potential. In this case, therefore, electron trajectories appear along which electrons travel to be caught by the vertical electric field without impinging on the gate.

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It has been found that if the electron emission position at which electrons are emitted from the emitter is shifted from the gate plane toward the anode plane (see Fig. 6), emitted electrons can form trajectories such as to be caught by the vertical electric field with substantially no possibility of impinging on the gate when the lateral electric field and the vertical electric field are approximately equal in strength, that is, the ratio of the strength of the lateral electric field to that of the vertical electric field is approximately 1 to 1.

Also, a study made of the electric field ratio has shown that if the distance between the gate electrode 144 and the extreme end of the emitter electrode 145 is d; the potential difference (between the gate electrode and the emitter electrode) when the device is driven is V1; the distance between the anode and the substrate (element) is H; and the potential difference between the anode and the cathode (emitter electrode) is V2, a trajectory along which electrons drawn out impinge on the gate is formed when the lateral electric field E1 =

V1/d is 50 times or more stronger than the vertical electric field E2 = V2/H.

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The inventor of the present invention has also found that a height s (defined as the distance between a plane containing a portion of a gate electrode 2 surface and substantially parallel to a substrate 1 surface and a plane containing an electron-emitting member 4 surface and substantially parallel to the substrate 1 surface (see Fig. 6)) can be determined such that substantially no scattering occurs on the gate electrode 2. The height s depends on the ratio of the vertical electric field and the lateral electric field (vertical electric field strength/lateral electric field strength). As the vertical-lateral electric field ratio is lower, the height s is lower. As the lateral electric field is stronger, the necessary height s is higher.

The height set in a practical manufacturing process ranges from 10~nm to $10~\text{\mu m}$.

In the conventional arrangement shown in Fig. 14, the gate 144 and the emitter (142, 145) are formed flush with each other along a common plane and the lateral electric field is stronger than the vertical electric field by an order of magnitude, so that there is a considerable tendency to reduce, by impingement on the gate, the amount of electrons drawn out into the vacuum.

Further, in the conventional arrangement, the structure of the device is determined so as to increase the strength of the electric field in the lateral direction, so that the electron distribution on the anode 146 spreads widely.

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As described above, to restrict the distribution of electrons reaching the anode 146, it is necessary (1) to reduce the drive voltage (Vf), (2) to unidirectionally draw out electrons, (3) to consider the trajectory of electrons and, if scattering on the gate occurs, (4) to consider the electron scattering mechanism (elastic scattering in particular).

Therefore the present invention aims to provide an electron-emitting device in which the distribution of electrons with which the anode surface is irradiated is made finer, and in which the electron emission efficiency is improved (the amount of emitted electrons absorbed in the gate electrode is reduced).

The structure of a novel electron-emitting device in accordance with the present invention will now be described below in detail.

Fig. 1A is a schematic plan view showing an example of an electron-emitting device in accordance with the present invention. Fig. 1B is a cross-sectional view taken along the line 1B-1B of Fig. 1A.

Fig. 6 is schematic cross-sectional view of the electron-emitting apparatus of the present invention in

a state where the electron-emitting apparatus having an anode disposed above the electron-emitting device of the present invention is being driven.

In Figs. 1A, 1B and 6 are illustrated an insulating substrate 1, an extraction electrode 2 (also referred to as "gate electrode" or "second electrode"), a cathode 3 (also referred to as "first electrode"), an electron-emitting material 4 provided on the cathode 3 (also referred to as "electron-emitting member" or "emitter material"), and an anode 61 (also referred to as "third electrode").

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In the electron-emitting apparatus of the present invention, if as shown in Figs. 1A, 1B and 6 the distance by which the cathode 3 and the gate electrode 2 are spaced apart from each other is d; the potential difference (the voltage between the cathode 3 and the gate electrode 2) when the electron-emitting device is driven is Vf; the distance between the anode 61 and the surface of the substrate 1 on which the electron-emitting device is arranged is H; and the potential difference between the anode 61 and the cathode 3 is Va, an electric field produced to drive the device (lateral electric field): E1 = Vf/d is set within the range from 1 to 50 times an electric field between the anode and the cathode (vertical electric field): E2 = Va/H.

The proportion of electrons impinging on the gate

electrode 2 in electrons emitted from the cathode 3 is reduced thereby. In this manner, a high-efficiency electron-emitting device capable of preventing an emitted electron beam from spreading out widely can be obtained.

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The "lateral electric field" referred to in the description of the present invention can also be expressed as "electric field in a direction substantially parallel to the surface of substrate 1". It can also be expressed as "electric field in the direction in which the gate 2 is opposed to the cathode 3".

Also, the "vertical electric field" referred to in the description of the present invention can also be expressed as "electric field in a direction substantially perpendicular to the surface of substrate 1". It can also be expressed as "electric field in the direction in which the substrate 1 is opposed to the anode 61".

Further, in the electron-emitting apparatus of the present invention, a plane containing the surface of the electron-emitting member 4 and substantially parallel to the surface of the substrate 1 is spaced apart from a plane containing a portion of the surface of the gate electrode 2 and substantially parallel to the surface of the substrate 1 (see Fig. 6). In other words, in the electron-emitting apparatus of the

present invention, a plane containing the surface of the electron-emitting member 4 and substantially parallel to the surface of the substrate 1 is placed between the anode 61 and a plane containing a portion of the surface of the gate electrode 2 and substantially parallel to the substrate surface (see Fig. 6).

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Further, in the electron-emitting device of the present invention, the electron-emitting member 4 is placed at a height s (defined as the distance between the plane containing a portion of the surface of gate electrode 2 and substantially parallel to the surface of substrate 1 and the plane containing the surface of electron-emitting member 4 and substantially parallel to the surface of substrate 1 (see Fig. 6)) such that substantially no scattering occurs on the gate electrode 2.

The height's depends on the ratio of the vertical electric field and the lateral electric field (vertical electric field strength/lateral electric field strength). As the vertical-lateral electric field ratio is lower, the height's is lower. As the lateral electric field is stronger, the necessary height's is higher. Practically, the height is not less than 10 nm not more than 10 μ m.

Examples of the insulating substrate 1 are the following substrates whose surfaces are sufficiently cleansed: quartz glass; glass in which the content of

an impurity such as Na is reduced by partial substitution by K, for example; a laminate formed in such a manner that SiO₂ is laminated by sputtering or the like on soda lime glass, a silicon substrate or the like; and an insulating substrate made of a ceramic such as alumina.

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is an electrically conductive member formed on the surface of the substrate 1 by an ordinary vacuum film forming technique, such as evaporation or sputtering, or a photolithography technique so as to face each other. The material of the electrodes 2 and 3 is selected from, for example, carbon, metals, nitrides of metals, carbides of metals, borides of metals, semiconductors, and metallic compounds of semiconductors. The thickness of the electrodes 2 and 3 is set within the range from several ten nanometers to several ten microns. Preferably, the material of the electrodes 2 and 3 is a heat resistant material formed of carbon, a metal, a nitride of a metal or a carbide of a metal.

The material of the electrodes 2 and 3 constituting the electron-emitting device in accordance with the present invention are disposed on the surface of the substrate 1. Needless to say, the extraction electrode 2 and the cathode 3 are spaced apart from each other along a direction substantially parallel to

the plane containing the surface of the substrate 1.

In other words, the electron-emitting device is constructed so that the extraction electrode 2 and the cathode 3 do not overlap each other.

In particular, in the case of growth of fibrous carbon described below, the electrodes are preferably formed of silicon having conductivity, e.g., doped polysilicon or the like.

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If there is apprehension about, for example, a voltage drop due to the small thickness of the electrodes, or if a plurality of the electron-emitting devices are used in matrix form, a low-resistance wiring metallic material may be used to form suitable wiring portions on condition that it does not affect emission of electrons.

The emitter material (electron-emitting member) 4 may be formed in such a manner that a film deposited by an ordinary vacuum film forming method such as sputtering is worked into the shape of the emitter by using a technique such as reactive ion etching (RIE). Alternatively, it may be formed by growing needle crystals or whiskers by seed growth in chemical vapor deposition (CVD). In the case of RIE, the control of the emitter shape depends on the kind of the substrate used, the kind of gas, the gas pressure (flow rate), the etching time, the energy for forming plasma, etc. In a CVD forming process, the emitter shape is

controlled by selecting the kind of the substrate, the kind of gas, the flow rate, the growth temperature, etc.

Examples of the material used to form the emitter (electron-emitting member) 4 are carbides, such as TiC, ZrC, HfC, TaC, SiC, and WC, amorphous carbon, graphite, diamondlike carbon, carbon containing dispersed diamond, and carbon compounds.

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According to the present invention, fibrous carbon is particularly preferably used as the material of the emitter (electron-emitting member) 4. "Fibrous carbon" referred to in the description of the present invention can also be expressed as "material in columnar form containing carbon as a main constituent" or "material in filament form containing carbon as a main constituent". Further, "fibrous carbon" can also be expressed as "fibers containing carbon as a main constituent". More specifically, "fibrous carbon" in accordance with the present invention comprises carbon nanotubes, graphite nanofibers, and amorphous carbon fibers. In particular, graphite nanofibers are most preferred as electron-emitting member 4.

The gap between the extraction electrode 2 and the cathode 3 and the drive voltage (the voltage applied between the extraction electrode 2 and the cathode 3) may be determined so that the value of the lateral electric field necessary for emission of electrons from

the cathode material used is 1 to 50 times larger than that of the vertical electric field necessary for forming an image, as described above.

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In a case where a light-emitting member such as a phosphor is provided on the anode, the necessary vertical electric field is, preferably, within the 10⁻¹ to 10 V/µm range. For example, in a case where the gap between the anode and the cathode is 2 mm and 10 kV is applied between the anode and the cathode, the vertical electric field is 5 V/µm. In this case, the emitter material (electron-emitting member) 4 to be used has an electron-emitting electric field value of 5 V/µm or higher. The gap and the drive voltage may be determined in correspondence with the selected electron-emitting electric field value.

An example of a material having an electric field threshold of several V/µm is fibrous carbon. Each of Figs. 11 and 12 shows an example of the configuration of fibrous carbon. In each of Figs. 11 and 12, the configuration is schematically shown at the optical microscope level (to 1,000 times) in the left-hand section, at the scanning electron microscope level (to 30,000 times) in the middle section, and at the transmission electron microscope level (to 1,000,000 times) in the right-hand section.

A graphene structure formed into a cylinder such as that shown in Fig. 11 is called a carbon nanotube (a

multilayer cylindrical graphene structure is called a multiwall nanotube). Its threshold value is minimized when the tube end is opened.

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The fibrous carbon shown in Fig. 12 may be produced at a comparatively low temperature. Fibrous carbon having such a configuration is composed of a graphene layered body (thus, it may be referred to as "graphite nanofiber", and has an amorphous structure whose ratio is increased with temperature). More specifically, "graphite nanofiber" designates a fibrous substance in which graphenes are layered (laminated) in the longitudinal direction thereof (in the axis direction of the fiber). In other words, graphite nanofiber is a fibrous substance in which a plurality of graphenes are arranged and layered (laminated) so as not to be parallel to the fiber axis, as shown in Fig. 12.

On the other hand, a carbon nanotube is a fibrous substance in which graphenes are arranged (in cylindrical shape) around the longitudinal direction (fiber axis direction). In other words, it is a fibrous substance in which graphenes are arranged substantially parallel to the fiber axis.

One layer of graphite is called "graphene" or "graphene sheet". More specifically, graphite is formed in such a manner that carbon planes on which carbon atoms are arrayed so as to form regular hexagons

close to each other by covalent bond in sp² hybridization are laid one on another while being spaced by a distance of 3.354Å. Each carbon plane is called "graphene" or "graphene sheet".

Each type of fibrous carbon has an electron emission threshold value of about 1 to 10 V/µm and is therefore preferred as the material of the emitter (electron-emitting member) 4 in accordance with the present invention.

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In particular, electron-emitting devices using graphite nanofibers, not limited to the device structure of the present invention shown in Fig. 1, etc., are capable of causing emission of electrons in a low electric field to obtain a large emission current, and can be readily manufactured to obtain as an electron-emitting device having stable electronemitting characteristics. For example, such an electron-emitting element can be obtained by forming graphite nanofibers as an emitter and by providing an electrode for controlling emission of electrons from the emitter. Further, if a light emitting member capable of emitting light when irradiated with electrons emitted from graphite nanofibers is used, a light emitting device such as a lamp can be formed. Further, an image display apparatus may be constructed

by forming an array of a plurality of the abovedescribed electron-emitting devices and by preparing an anode having a light emitting material such as a phosphor. In the electron-emitting device, the light emitting device or the image display apparatus using above-described graphite nanofibers, stable emission of electrons can be achieved without maintaining inside the device or the apparatus an ultrahigh vacuum such as that required in conventional electron-emitting devices. Moreover, since electrons are emitted by a low electric field, the device or apparatus can be easily manufactured with improved reliability.

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The above-described fibrous carbon can be formed by decomposing a hydrocarbon gas by using a catalyst (a material for accelerating deposition of carbon). The processes for forming carbon nanotubes and graphite nanofibers differ in the kind of catalyst and decomposition temperature.

The catalytic material may be a material which is used as a seed for forming fibrous carbon, and which is selected from Fe, Co, Pd, No, and alloys of some of these materials.

In particular, if Pd or Ni is used, graphite nanofibers can be formed at a low temperature (not lower than 400°C). The necessary carbon nanotube forming temperature in the case of using Fe or Co is 800°C or higher. Also, the process of producing a graphite nanofiber material by using Pd or Ni, which can be performed at a lower temperature, is preferred

from the viewpoint of reducing the influence on other components and limiting the manufacturing cost.

Further, the characteristic of Pd that resides in enabling oxides to be reduced by hydrogen at a low temperature (room temperature) may be utilized. That is, palladium oxide may be used as a seed forming material.

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If hydrogen reduction using palladium oxide is performed, an initial agglomeration seed can be formed at a comparatively low temperature (equal to or lower than 200°C) without metallic film thermal agglomeration or ultrafine particle forming/deposition conventionally used as ordinary seed forming techniques.

The above-mentioned hydrocarbon gas may be, for example, acetylene, ethylene, methane, propane, or propylene. Further, CO or CO₂ gas or vapor of an organic solvent such as ethanol or acetone may be used in some case.

In the device of the present invention, the region where the emitter (electron-emitting member) exists will be referred to as "emitter region" regardless of contribution to emission of electrons.

The position of the electron emission point (electron-emitting portion) in the "emitter region" and the electron-emitting operation will be described with reference to Figs. 6 and 7.

The electron-emitting device having the distance

between the cathode 3 and the extraction electrode 2 to several microns was set in a vacuum apparatus 60 such as shown in Fig. 6. A sufficiently high degree of vacuum about 10⁻⁴ Pa was produced by a evacuating pump 65. A potential (voltage Va) higher by several kilovolts than that of the cathode 3 and the extraction electrode was applied from a voltage source ("second voltage application means" or "second potential application means") to the anode 61, which was placed so that the surface of the anode 61 is at the height H, which was several millimeters, from the surface of the substrate 1, as shown in Fig. 6. While the voltage Va was applied between the cathode 3 and the anode 61, the voltage applied to the anode may be a voltage from the ground potential. The substrate 1 and the anode 61 were positioned relative to each other so that their surfaces are parallel to each other.

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Between the cathode 3 and the extraction electrode 2 of the electron-emitting device, a voltage of about several ten volts was applied as drive voltage Vf from a power supply (not shown) ("first voltage application means" or "first potential application means"). Device current If flowing between the electrodes 2 and 3 and electron emission current Ie flowing through the anode were measured.

It is supposed that, during this operation, equipotential lines 63 are formed as shown in Fig. 6

(an electric field (the direction of an electric field) substantially parallel to the surface of the substrate 1, and that the concentration of the electric field is maximized at the point on a portion of the electronemitting member 4 closest to the anode and facing the gap, as indicated by 64. It is thought that electrons are emitted mainly from the portion of the electronemitting material in the vicinity of this electric field concentration point, where the concentration of the electric field is maximized. An Ie characteristic such as shown in Fig. 7 was obtained. That is, Ie rises abruptly at a voltage about half the applied The If characteristic (not shown) was similar voltage. to the Ie characteristic but the value of If was sufficiently smaller than that of Ie.

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An electron source obtained by arranging a plurality of the electron-emitting devices in accordance with the present invention will be described with reference to Fig. 8. In Fig. 8 are illustrated an electron source substrate 81, X-direction wiring 82, Y-direction wiring 83, electron-emitting device 84 in accordance with the present invention, and a connecting conductor 85.

X-direction wiring 82 has m conductors DX1, DX2,

... DXm, which may be constituted by, for example, a
conductive metal formed by vacuum evaporation,
printing, sputtering, or the like. The material, film

thickness, and width of the wiring are selected according to a suitable design. Y-direction wiring 83 has n conductors DY1, DY2, ... DYn and is formed in the same manner as X-direction wiring 82. An interlayer insulating layer (not shown) is provided between the m conductors of X-direction wiring 82 conductors and the n conductors of Y-direction wiring 83 to electrically separate these conductors (each of m and n is a positive integer).

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The interlayer insulating layer (not shown) is, for example, a SiO₂ layer formed by vacuum evaporation, printing, sputtering, or the like. For example, the interlayer insulating film is formed in the desired shape over the whole or part of the surface of the substrate 81 on which X-direction wiring 82 has been formed and the film thickness, material and fabrication method are selected to ensure withstanding against the potential difference at the intersections of the conductors of X-direction wiring 82 and Y-direction wiring 83 in particular. The conductors of X-direction wiring 82 and Y-direction wiring 83 are respectively extended outward as external terminals.

Pairs of electrodes (not shown) constituting electron-emitting devices 84 are electrically connected to the m conductors of X-direction wiring 82 and the n conductors of Y-direction wiring 83 by connecting conductors 85 made of a conductive metal or the like.

The materials forming wiring 82 and wiring 83, the material forming the connecting conductors 85 and the materials forming the pairs of device electrodes may be entirely constituted of common constituent elements or partially constituted of common constituent elements, or may be constituted of different constituent elements. These materials are selected from, for example, the above-described device electrode materials. If the materials of the device electrodes and the wiring materials are the same, the wiring conductors connected to the device electrodes can be considered to be device electrodes.

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A scanning signal application means (not shown) for applying scanning signals for selecting the rows of electron-emitting devices 84 arranged in the X-direction is connected to X-direction wiring 82. On the other hand, a modulation signal generation means for modulating voltages applied to the columns of electron-emitting devices 84 arranged in the Y-direction according to input signals is connected to Y-direction wiring 83. The drive voltage applied to each electron-emitting device is supplied as a voltage corresponding to the difference between the scanning signal and the modulation signal applied to the element.

In the above-described arrangement, each device can be selected by using the passive-matrix wiring to

be driven independently.

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An image forming apparatus constructed by using an electron source having such a passive matrix array will be described with reference to Fig. 9. Fig. 9 schematically shows an example of the display panel of the image forming apparatus. Referring to Fig. 9, a plurality of electron-emitting devices are disposed on an electron source substrate 81, which is fixed on a rear plate 91. A face plate 96 has a glass substrate 93, a phosphor film 94 provided as a light emitting member on the internal surface of the glass substrate 93, a metal back (anode) 95, etc. The rear plate 91 and the face plate 96 are connected to a supporting frame 92 by using frit glass or the like. An envelop 97 is formed by being seal-bonded by baking in, for example, atmospheric air, a vacuum or in nitrogen in the 400 to 500°C temperature range for 10 minutes or longer.

20 by the face plate 96, the supporting frame 92, and the rear plate 91. The rear plate 91 is provided mainly for the purpose of reinforcing the substrate 81. If the substrate 81 itself has sufficiently high strength, there is no need to separately provide the rear plate 91. That is, the supporting frame 92 may be directly seal-bonded to the substrate 81 and the envelop 97 may be formed by the frame plate 96, the supporting frame

92 and the substrate 81. A supporting member (not shown) called a spacer may be provided between the face plate 96 and the rear plate 91 to enable the envelop 97 to have a sufficiently high strength for resisting atmospheric pressure.

Embodiments of the present invention will be described below in detail.

(Embodiment 1)

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Fig. 1A shows a top view of an electron-emitting

device fabricated in this embodiment. Fig. 1B is a

cross-sectional view taken along the line 1B-1B of Fig.

1A.

Figs. 1A and 1B illustrate an insulating substrate

1, an extraction electrode 2 (gate), a cathode 3, and

an emitter material 4.

The process of fabricating the electron-emitting device of this embodiment will be described in detail. (Step 1)

A quartz substrate was used as substrate 1. After sufficiently cleansing the substrate, a 5 nm thick Ti film (not shown) and a 30 nm thick poly-Si film (arsenic doped) were successively deposited by sputtering on the substrate as gate electrode 2 and cathode 3.

Next, a resist pattern was formed by photolithography using a positive photoresist (AZ1500/from Clariant Corporation).

Thereafter, dry etching was performed on the poly-Si (arsenic doped) layer and Ti layer with the patterned photoresist used as a mask, CF₄ gas being used to etch the Ti layer. An extraction electrode 2 and a cathode 3 having a gap of 5 µm therebetween were thereby formed (Fig. 5A).

(Step 2)

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Next, a Cr having a thickness of about 100 nm was deposited on the entire substrate by electron beam (EB) evaporation.

A resist pattern was formed by photolithography using a positive photoresist (AZ1500/ from Clariant Corporation).

An opening corresponding to a region (100 µm square) where electron-emitting material 4 was to be provided was formed on the cathode 3 with the patterned photoresist used as a mask. Cr at the opening was removed by using a cerium nitrate etching solution.

After removing the resist, a complex solution prepared by adding isopropyl alcohol, etc., to a Pd complex was applied to the entire substrate by spin coating.

After application of the solution, a heat treatment was performed in atmospheric air at 300°C to form a palladium oxide layer 51 having a thickness of about 10 nm. Thereafter, Cr was removed by using a cerium nitrate etching solution (Fig. 5B).

(Step 3)

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The substrate was baked at 200°C, atmospheric air was evacuated, and a heat treatment was then performed in 2% hydrogen flow diluted with nitrogen. At this stage, particles 52 having a diameter of about 3 to 10 nm were formed on the surface of the cathode 3. The density of the particles at this stage was estimated at about 10¹¹ to 10¹² particles/cm² (Fig. 5C). (Step 4)

Subsequently, a heat treatment was performed in a 0.1% ethylene flow diluted with nitrogen at 500°C for

10 minutes. The state after the heat treatment was observed with a scanning electron microscope to find that a multiplicity of fibrous carbon 4 having a diameter of about 10 to 25 nm and extending like fiber

diameter of about 10 to 25 nm and extending like fibers while curving or bending had been formed in the Pd-coated region. The thickness of the fibrous carbon layer was about 500 nm (Fig. 5D).

vacuum apparatus 60 shown in Fig. 6. A sufficiently high vacuum of about 2×10⁻⁵ Pa was produced by the evacuating pump 62. Voltage Va = 10 kV was applied as anode voltage to the anode 61 distanced by H = 2 mm from the device, as shown in Fig. 6. Also, a pulse voltage of Vf = 20 V was applied as drive voltage to the device. Device current If and electron emission current Ie thereby caused were measured.

The If and Ie characteristics of the electronemitting device were as shown in Fig. 7. That is, Ie
rises abruptly at a voltage about half the applied
voltage, and a current of about 1µA was measured as
electron emission current Ie at a Vf value of 15 V. On
the other hand, the If characteristic was similar to
the Ie characteristic but the value of If was smaller
than that of Ie by an order of magnitude or more.

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Gap: 5 µm

The obtained beam had a generally rectangular shape having a longer side along the Y-direction and a shorter side in the X-direction. The beam width was measured with respect to different gaps of 1 µm and 5 µm between the electrodes 2 and 3 while Vf was fixed at 15 V and the distance H to the anode was fixed at 2 mm. Table 1 shows the results of this measurement.

Va = 5 kV Va = 10 kV

Gap: 1 μ m 60 μ m in x-direction 30 μ m in x-direction 170 μ m in y-direction 150 μ m in y-direction

72 µm in x-direction

150 µm in y-direction

93 µm in x-direction

170 µm in y-direction

It was possible to change the necessary electric field for driving by changing the fibrous carbon growth conditions. In particular, the average particle size of Pd particles formed by reduction of palladium oxide

is related to the diameter of fibrous carbon thereafter grown. It was possible to control the average Pd particle size through the Pd density in the Pd complex coating and the rotational speed of spin coating.

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The fibrous carbon of this electron-emitting device was observed with the transmission electron microscope to recognize a structure in which graphenes are layered in the fiber axis direction, as shown in the right-hand section of Fig. 12. The graphene stacking intervals (in the Z-axis direction) resulting from heating at a lower temperature, about 500°C were indefinite and was 0.4 nm. As the heating temperature was increased, the grating intervals became definite. The intervals resulting from heating at 700°C were 0.34 nm, which is close to 0.335 nm in graphite. (Embodiment 2)

Fig. 2 shows a second embodiment of the present invention.

In this embodiment, an electron-emitting device was fabricated in the same manner as that in the first embodiment except that the cathode 3 corresponding to that in the first embodiment had a thickness of 500 nm and fibrous carbon provided as electron-emitting material 4 had a thickness of 100 nm. Currents If and Ie in the fabricated electron-emitting device were measured.

In this device arrangement, the electron emission

point was positively heightened (toward the anode) relative to the gate electrode by increasing the thickness of the cathode 3. Trajectories along which electrons impinge on the gate were thereby reduced, thereby preventing a reduction in efficiency and occurrence of a beam-thickening phenomenon.

Also in this device arrangement, the electron emission current Ie at Vf = 20V was about $1\mu A$. On the other hand, the If characteristic was similar to the Ie characteristic but the value of If was smaller than that of Ie by two orders of magnitude.

The results of measurement of the beam diameter in this embodiment were substantially the same as those shown in Table 1.

15 (Embodiment 3)

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Fig. 3 shows a third embodiment of the present invention.

In this embodiment, in the step corresponding to step 2 in the first embodiment, palladium oxide 51 was provided on the cathode 3 and in the gap between the electrodes 2 and 3. Pd oxide was provided in the gap in such a manner as to extend from the cathode 3 to a point near the midpoint of the gap. Excepting step 2, this embodiment is the same as the first embodiment.

The electric field in the electron-emitting device of this embodiment was twice as strong as that in the first embodiment because the gap was reduced, thereby enabling the drive voltage to be reduced to about 8 V.

(Embodiment 4)

Fig. 4 shows a fourth embodiment of the present invention. In this embodiment step 1 and step 2 described above with respect to the first embodiment are changed as described below.

(Step 1)

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A quartz substrate was used as substrate 1. After sufficiently cleansing the substrate, a 5 nm thick Ti film and a 30 nm thick poly-Si film (arsenic doped) were successively deposited by sputtering on the substrate as cathode 3.

Next, a resist pattern was formed by photolithography using a positive photoresist (AZ1500/from Clariant Corporation).

Next, dry etching was performed on the poly-Si layer and Ti layer by using CF₄ gas, with the patterned photoresist used as a mask. Cathode 3 was thereby formed.

The quartz substrate was then etched to a depth of about 500 nm by using a mixed acid formed of hydrofluoric acid and ammonium fluoride.

Subsequently, a 5 nm thick Ti film and a 30 nm thick Pt film were successively deposited on the substrate as gate electrode 2 by again performing sputtering. After removing the photoresist from the cathode, a resist pattern was again formed by using a positive photoresist (AZ1500/ from Clariant

Corporation) to form the gate electrode.

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Next, dry etching was performed on the Pt layer and Ti layer by using Ar, with the patterned photoresist used as a mask. Electrode 2 was thereby formed so that the step formed between the electrodes functions as a gap.

Next, a resist pattern was formed on the cathode, a Ni film having a thickness of about 5 nm was formed by resistance heating evaporation having a good straight-in effect, and oxidation was thereafter performed at 350°C for 30 minutes.

This step was followed by the same steps as those in the first embodiment.

The above-described device arrangement enabled formation of a finer gap such that electrons were effectively emitted at a lower voltage of about 6 V.

Because the height of the electron-emitting material 4 (film thickness) was increased relative to that of the gate electrode, electrons were drawn out not only from the upper portion of the electron-emitting material 4 but also from an intermediate portion. Thus, the arrangement in this embodiment has the effect of preventing a reduction in efficiency due to impingement of electrons on the gate electrode and occurrence of a beam-thickening phenomenon.

(Embodiment 5)

An electron source obtained by arranging a

plurality of the electron-emitting devices fabricated the first embodiment and an image forming apparatus using this electron source will be described with reference to Figs. 8, 9, and 10. In Fig. 8 are illustrated an electron source substrate 81, X-direction wiring 82, Y-direction wiring 83, electron-emitting devices 84 in accordance with the present invention, and connecting conductors 85.

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The electron source with matrix wiring shown in Fig. 8, in which the device capacitance is increased by arranging a plurality of electron-emitting devices, has a problem that, even when a short pulse produced by pulse-width modulation is applied, the waveform is dulled or distorted by capacitive components to cause failure to obtain the necessary grayscale level, for example. In this embodiment, therefore, a structure is adopted in which an interlayer insulating layer is provided by the side of the electron-emitting region to limit the increase in capacitive components in regions other than the electron-emitting region.

Referring to Fig. 8, X-direction wiring 82 has m conductors DX1, DX2, ... DXm, which has a thickness of about 1 µm and a width of 300 µm, and which is formed of an aluminum wiring material by evaporation. The material, film thickness, and width of the wiring conductors are selected according to a suitable design. Y-direction wiring 83 has n conductors DY1, DY2, ...

DYn, which has a thickness of 5 μ m and width of 100 μ m, and which is formed in the same manner as X-direction wiring 82. An interlayer insulating layer (not shown) is provided between the m conductors of X-direction wiring 82 and the n conductors of Y-direction wiring 83 to electrically separate these conductors (each of m and n is a positive integer).

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The interlayer insulating layer (not shown) is, for example, a SiO₂ layer formed by sputtering or the like and having a thickness of about 0.8 µm. For example, the interlayer insulating film is formed in the desired shape over the whole or part of the surface of the substrate 81 on which X-direction wiring 82 has been formed. Specifically, the thickness of the interlayer insulating film is determined so as to ensure withstanding against the potential difference at the intersections of the conductors of X-direction wiring 82 and Y-direction wiring 83. The conductors of X-direction wiring 82 and Y-direction wiring 83 are respectively extended outward as external terminals.

Pairs of electrodes (not shown) constituting electron-emitting devices 84 are electrically connected to the m conductors of X-direction wiring 82 and the n conductors of Y-direction wiring 83 by connecting conductors 85 made of a conductive metal or the like.

A scanning signal application means (not shown) for applying scanning signals for selecting the rows of

electron-emitting devices 84 arranged in the Xdirection is connected to X-direction wiring 82. the other hand, a modulation signal generation means for modulating voltages applied to the columns of electron-emitting devices 84 arranged in the Ydirection according to input signals is connected to Ydirection wiring 83. The drive voltage applied to each electron-emitting device is supplied as a voltage corresponding to the difference between the scanning signal and the modulation signal applied to the element. In the present invention, Y-direction wiring 83 is connected to the gate electrodes 2 of the electron-emitting devices described above with respect to the first embodiment, while X-direction wiring is connected to the cathodes 3 of the elements. connection realizes a beam convergence effect which characterizes the present invention.

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In the above-described arrangement, each element can be selected by using the passive-matrix wiring to be driven independently.

An image forming apparatus constructed by using an electron source having such a passive matrix array will be described with reference to Fig. 9. Fig. 9 is a diagram showing the display panel of the image forming apparatus.

Referring to Fig. 9, the electron source having the plurality of electron-emitting devices described

above with reference to Fig. 8 is provided on an electron source substrate 81. The substrate 81 is fixed on a rear plate 91. A face plate 96 has a glass substrate 93, a phosphor film 94 provided as a light emitting member on the internal surface of the glass substrate 93, a metal back 95, etc. The rear plate 91 and the face plate 96 are connected to a supporting frame 92 by using frit glass or the like. An envelop 97 is formed by being seal-bonded by baking in a vacuum at about a temperature of 450°C for 10 minutes. The electron-emitting devices 84 correspond to the electron-emitting regions shown in Fig. 9. X-direction wiring 82 and Y-direction wiring 83 are connected to the pairs of electrodes of the electron-emitting elements in this embodiment.

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The envelop 97, as described above, is constituted by the face plate 96, the supporting frame 92, and the rear plate 91. A supporting member (not shown) called a spacer is provided between the face plate 96 and the rear plate 91 to enable the envelop 97 to have a sufficiently high strength for resisting atmospheric pressure.

After fabrication of the phosphor film, the metal back 95 is made by smoothing the inner surface of the phosphor film (ordinarily called "filming") and by thereafter depositing Al by vacuum evaporation or the like.

The face plate 96 further has a transparent electrode (not shown) provided on outer surface of the phosphor film 94 to improve the conductivity of the phosphor film 94.

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The scanning circuit 102 will be described. The scanning circuit 102 includes M switching devices (schematically shown as S1 to Sm in the figure). of the switching devices S1 to Sm selects one of the output voltage from a direct-current voltage source Vx and 0 (V) (ground level). The switching devices S1 to Sm are respectively connected to terminals Dx1 to Dxm of the display panel 101. Each of the switching devices S1 to Sm operates on the basis of a control signal Tscan output from a control circuit 103, and may be a combination of a switching device such as a fieldeffect transistor (FET) and other components. In this example, the direct-current voltage source Vx is configured to output a constant voltage such that the drive voltage to be applied to a device which is not scanned on the basis of characteristics of the electron-emitting device (electron emitting threshold value voltage), is not higher than the electronemitting threshold value voltage.

The control circuit 103 has the function of matching the operations of the components with each other to suitably perform display on the basis of input signals externally supplied. The control circuit 103

generates control signals Tscan, Tsft, and Tmry to the components on the basis of sync signal Tsync supplied from a sync signal separation circuit 106.

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The sync signal separation circuit 106 is a circuit for separating sync signal components and luminance signal components from an NTSC television signal externally supplied. This circuit can be formed by using an ordinary frequency separation (filter) circuit, etc. The sync signal separated by the sync signal separation circuit 106 is formed of a vertical sync signal and a horizontal sync signal. However, it is shown as Tsync in the figure for convenience sake. Image luminance signal components separated from the television signal are shown as DATA signal for convenience sake. The DATA signal is input to a shift register 104.

The shift register 104 is a device for serial to parallel conversion, with respect to each image line, of the DATA signal which is input in time sequence.

20 The shift register 104 operates on the basis of control signal Tsft supplied from the control circuit 103.

(That is, control signal Tsft may be considered to be a shift clock for the shift register.) Data corresponding to one image line after serial to

25 parallel conversion (corresponding to data for driving N electron-emitting devices) is output as N parallel signals Idl to Idn from the shift register 104.

The line memory 105 is a storage device for storing data corresponding to one image line for a necessary time period. The line memory 105 stores the contents of the signals Idl to Idn according to control signal Tmry supplied from the control circuit 103. The stored contents are output as I'dl to I'dn to be input to a modulation signal generator 107.

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The modulation signal generator 107 is a signal source for suitably modulating signals for driving the electron-emitting devices according to image data items I'dl to I'dn. Output signals from the modulation signal generator 107 are applied to the electron-emitting devices in the display panel 111 through terminals Doyl to Doyn.

As described above, each electron-emitting device to which the present invention can be applied has basic characteristics described below with respect to emission current Ie. That is, there is a definite threshold value voltage Vth with respect to emission of electrons. Emission of electrons is caused only when a voltage higher than Vth is applied. When a voltage higher than the electron emission threshold value is applied to the electron-emitting device, the emission current changes according to changes in the applied voltage. Therefore, in a case where a voltage in the form of pulses is applied to the electron-emitting device, electron emission is not caused when the value

of the applied voltage is lower than the electron emission threshold value, but an electron beam is output when the value of the applied voltage is equal to or higher than the electron emission threshold value. In this case, the strength of the electron beam can be controlled by changing the pulse crest value Vm. Also, the total amount of charge of the output electron beam can be controlled by changing the pulse width Pw.

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Therefore, a voltage modulation method, a pulse-width modulation method or the like can be used as a method for modulating the electron-emitting device according to the input signal. If the voltage modulation method is carried out, a voltage modulation type of circuit capable of generating voltage pulses having a constant duration, and modulating the pulse crest value according to input data may be used as modulation signal generator 107.

If the pulse-width modulation method is carried out, a pulse-width modulation type of circuit capable of generating voltage pulses having a constant crest value and modulating the pulse width of the voltage pulses according to input data may be used as modulation signal generator 107.

Each of the shift register 104 and the line memory 105 used in this embodiment is of a digital signal type.

In this embodiment, a digital to analog converter

circuit, for example, is used in the modulation signal generator 107 and an amplifier circuit, etc., are added if necessary. For example, in the case where the pulse-width modulation method is used, a combination of a high-speed oscillator, a counter for counting the number of waves output from the oscillator, and a comparator for comparing the output value of the counter and the output value of the above-described memory is used in the modulation signal generator 107.

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The configuration of the image forming apparatus described above is an example of the image forming apparatus to which the present invention can be applied. Various modifications and changes can be made therein on the basis of the technical spirit of the present invention. The input signal is not limited to the above-mentioned NTSC signal. Those in accordance with the PAL system and the SECAM system and other TV signals corresponding to a larger number of scanning lines (e.g., those for the MUSE system and other high-definition TV systems) may also be used.

Images were displayed on an image display apparatus made in accordance with this embodiment. High-luminance high-definition images had been displayed on the image display apparatus with stability for a long period of time.

According to the present invention, as described above, the specific capacitance of an electron-emitting

device can be reduced and the drive voltage can also be reduced. An electron source having improved efficiency and a smaller beam size can be realized by using such an electron-emitting device.

An image forming apparatus having high resolution, e.g., a color flat-screen television can be realized by using the electron-emitting device in accordance with the present invention.

WHAT IS CLAIMED IS:

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- 1. An electron-emitting apparatus comprising:
- A) a first electrode and a second electrode disposed on a surface of a substrate;
- B) first voltage application means for applying to said second electrode a potential higher than a potential applied to said first electrode;
 - C) an electron-emitting member disposed on said first electrode;
- D) a third electrode disposed so as to face said substrate, electrons emitted from said electron-emitting member reaching said third electrode; and
 - E) second voltage application means for applying to said third electrode a potential higher than each of the potentials applied to said first and second electrodes.

wherein a surface of said electron-emitting member is placed between a plane containing a surface of said second electrode and substantially parallel to the surface of said substrate and a plane containing a surface of said third electrode and substantially parallel to the surface of said substrate, and

wherein when the distance between said second electrode and said first electrode is d; the potential difference applied between said second electrode and said first electrode by said first voltage application means is V1; the distance between said third electrode

and said substrate is H; and the potential difference between the potential applied to said third electrode by said second voltage application means and the potential applied to said first electrode by said first voltage application means is V2, then an electric field E1 = V1/d is within the range from 1 to 50 times an electric field E2 = V2/H.

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- An apparatus according to claim 1, wherein the
 thickness of said first electrode is larger than the
 thickness of said second electrode.
 - 3. An apparatus according to claim 1, wherein said electron-emitting member extends from a position on said first electrode to a position on said substrate between said first electrode and said second electrode.
 - 4. An apparatus according to claim 1, wherein said substrate has a difference in level between said second electrode and said first electrode, and said third electrode is closer to said first electrode than to said second electrode.
- 5. An apparatus according to claim 1, wherein said electron-emitting member is made of a material containing carbon as a main ingredient.

- 6. An apparatus according to claim 5, wherein said material containing carbon as a main ingredient comprises fibrous carbon.
- 7. An apparatus according to claim 6, wherein said fibrous carbon comprises a graphite nanofiber, a carbon nanotube, amorphous carbon, or a mixture of at least two of these materials.
- 8. An apparatus according to claim 7, wherein said fibrous carbon is grown by means of catalytic particles.
- 9. An apparatus according to claim 8, wherein
 15 catalytic particles are made of Pd, Ni, Fe, Co or an alloy of at least two of these metals.

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- 10. An apparatus according to any one of claims 1 to 9, wherein a plurality of said first electrodes and a plurality of said second electrodes are disposed on the surface of said substrate.
- 11. An apparatus according to claim 10, wherein said plurality of first electrodes and said plurality of second electrodes are electrically connected to wiring in matrix form.

12. An apparatus according to claim 10, wherein a phosphor capable of emitting light when irradiated with electrons emitted from said electron-emitting member is provided on said third electrode.

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- 13. An image display apparatus using an electronemitting apparatus according to claim 12.
 - 14. An electron-emitting device comprising:
- A) a fiber containing carbon as a main ingredient; and
 - B) an electrode for controlling emission of electrodes from said fiber containing carbon as a main ingredient,
- wherein said fiber containing carbon as a main ingredient has a plurality of graphenes layered so as not to be parallel to the axis direction of said fiber.
- 15. An electron-emitting device according to 20 claim 14, wherein the plurality of graphenes are substantially parallel to each other.
 - 16. An electron-emitting device according to claim 14, further comprising a cathode, wherein said fiber containing carbon as a main ingredient is provided on said cathode and is electrically connected to said cathode.

- 17. An electron-emitting device according to claim 16, wherein said cathode and said electrode for controlling emission of electrons are disposed on one substrate, a gap being formed between said cathode and said electrode for controlling emission of electrons.
- 18. An electron-emitting device according to claim 14, wherein said electron-emitting device comprises a plurality of said fibers containing carbon as a main ingredient.
 - 19. A light-emitting apparatus comprising an electron-emitting device according to any one of claims14 to 18, and a light-emitting member.

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- 20. An image display apparatus comprising a plurality of electron-emitting devices and a light emitting member capable of emitting light when irradiated with electrons emitted from some of said plurality of electron-emitting devices, wherein each of said plurality of electron-emitting devices is constituted by the electron-emitting device according to any one of claims 14 to 18.
- 25 21. An electron-emitting apparatus comprising:
 - A) a first electrode and a second electrode disposed on a surface of a substrate;

- B) first voltage application means for applying to said second electrode a potential higher than a potential applied to said first electrode;
- C) a plurality of fibers disposed on said first electrode, said fibers containing carbon as a main constituent;
- D) a third electrode disposed so as to face said substrate, electrons emitted from said fibers reaching said third electrode; and
- E) second voltage application means for applying to said third electrode a potential higher than each of the potentials applied to said first and second electrodes,

wherein a surface region of said fibers is placed between a plane containing a surface of said second electrode and substantially parallel to the surface of said substrate and a plane containing a surface of said third electrode and substantially parallel to the surface of said substrate.

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22. An electron-emitting apparatus according to claim 21, wherein when the distance between said second electrode and said first electrode is d; the potential difference applied between said second electrode and said first electrode by said first voltage application means is V1; the distance between said third electrode and said substrate is H; and the potential difference

between the potential applied to said third electrode by said second voltage application means and the potential applied to said first electrode is V2, then an electric field E1 = V1/d is within the range from 1 to 50 times an electric field E2 = V2/H.

23. An apparatus according to claim 21, wherein each of said fibers having carbon as a main ingredient comprises a carbon nanotube.

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- 24. An apparatus according to claim 21, wherein each of said fibers containing carbon as a main ingredient comprises a plurality of graphenes stacked so as to be nonparallel to the axis direction of said fiber.
- 25. An apparatus according to claim 21, wherein a material more effective in accelerating deposition of carbon than the material of said first electrode is provided between said fibers having carbon as a main ingredient and said cathode.
- 26. An apparatus according to claim 25, wherein said material effective in accelerating deposition of carbon comprises Pd, Ni, Fe, Co or an alloy formed of at least two of said metals.

27. An apparatus according to claim 25, wherein said material effective in accelerating deposition of carbon is provided in the form of a plurality of particles on said first electrode.

- 28. An apparatus according to claim 27, wherein said plurality of particles are provided on said first electrode at a density of 10^{10} particles/cm² or higher.
- 29. An apparatus according to claim 21, wherein the thickness of said first electrode is larger than the thickness of said second electrode.
- 30. An apparatus according to any one of claims
 21 to 29, wherein a plurality of said first electrodes
 and a plurality of said second electrodes are disposed
 on the surface of said substrate.
- 31. An apparatus according to claim 30, wherein said plurality of first electrodes and said plurality of second electrodes are electrically connected to wiring in matrix form.
- 32. An apparatus according to claim 30, wherein a phosphor capable of emitting light when irradiated with electrons emitted from said fibers is provided on said third electrode.

- 33. An image display apparatus using an electronemitting apparatus according to claim 32.
 - 34. An electron-emitting device comprising:
- A) a first electrode and a second electrode disposed on a surface of a substrate, a gap being formed between said first and second electrodes; and
 - B) a fiber provided on said first electrode, said fiber containing carbon as a main ingredient,

wherein said second electrode comprises an electrode for controlling emission of electrodes from said fiber containing carbon as a main ingredient, and

wherein said fiber containing carbon as a main ingredient comprises graphene.

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- 35. An electron-emitting device according to claim 34, wherein the distance between an extreme end of said fiber and the surface of said substrate is larger than the distance between the surface of said second electrode and the surface of said substrate.
- 36. An electron-emitting device according to claim 34, wherein said graphene comprises cylindrical graphene.

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37. An electron-emitting device according to claim 34, wherein said electron-emitting device

comprises a plurality of fibers containing carbon as a main ingredient.

- 38. A light-emitting apparatus comprising an electron-emitting device according to any one of claims 34 to 37, and a light-emitting member.
- 39. An image display apparatus comprising a plurality of electron-emitting devices and a light

 10 emitting member capable of emitting light when irradiated with electrons emitted from some of said plurality of electron-emitting devices, wherein each of said plurality of electron-emitting devices is constituted by an electron-emitting device according to any one of claims 34 to 37.

ABSTRACT OF THE DISCLOSURE

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An electron-emitting device in which the specific capacitance and the drive voltage are reduced, and which is capable of obtaining a finer electron beam by controlling the trajectory of emitted electrons. An electron-emitting portion of an electron-emitting member is positioned between the height of a gate and the height of an anode. When the distance between the gate and a cathode is d; the potential difference at driving the device is V1; the distance between the anode and the substrate is H; and the potential difference between the anode and the cathode is V2, then the electric field E1 = V1/d during driving is configured to be within the range from 1 to 50 times E2 = V2/H.

FIG. 1A

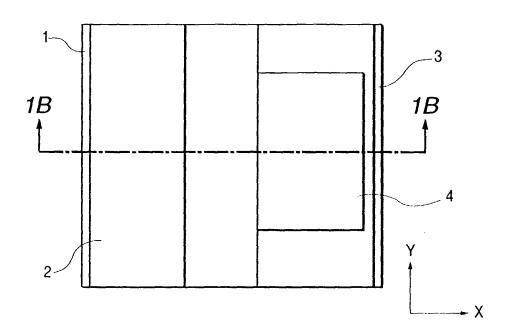


FIG. 1B

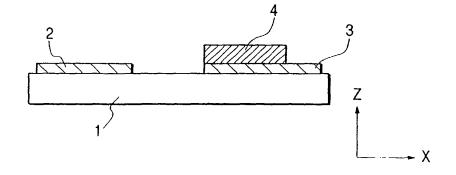


FIG. 2A

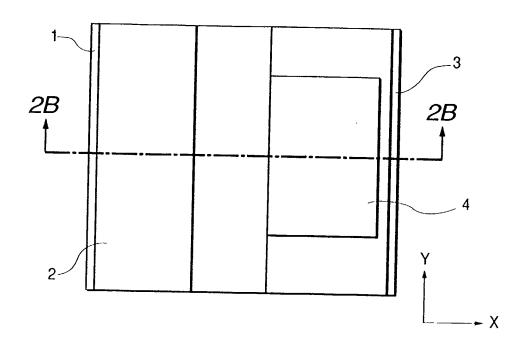


FIG. 2B

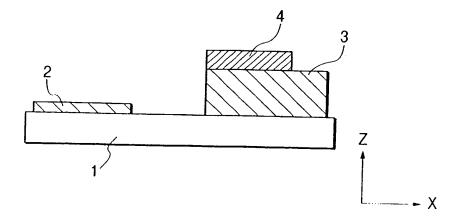


FIG. 3A

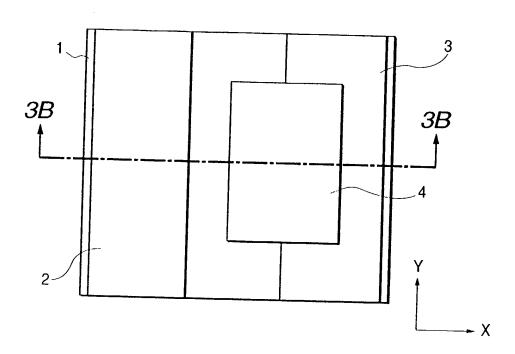


FIG. 3B

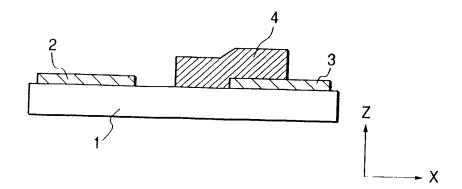


FIG. 4A

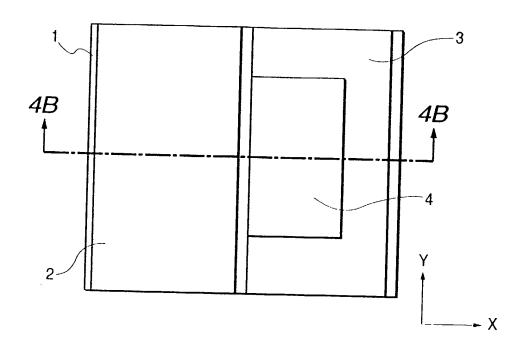
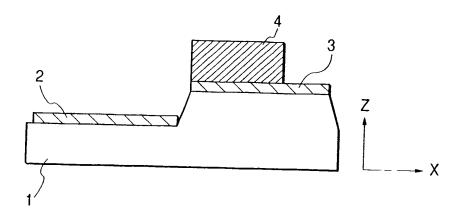


FIG. 4B



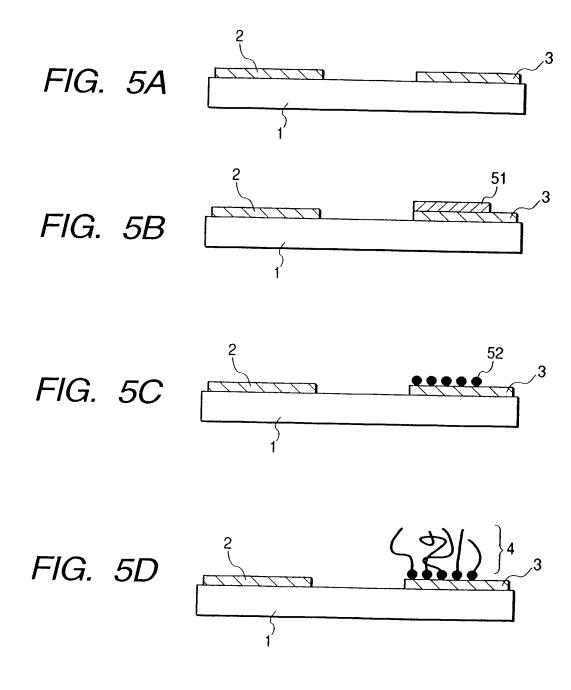


FIG. 6

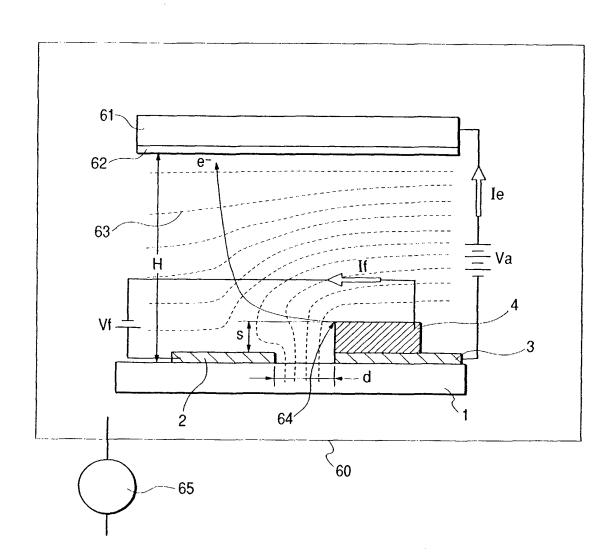


FIG. 7

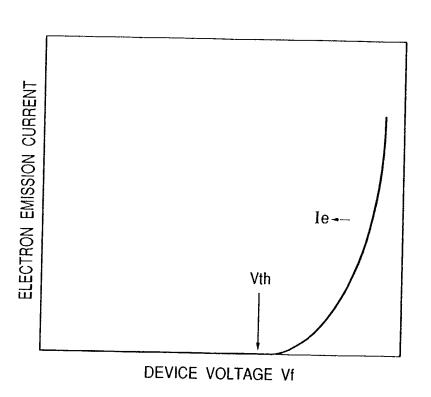
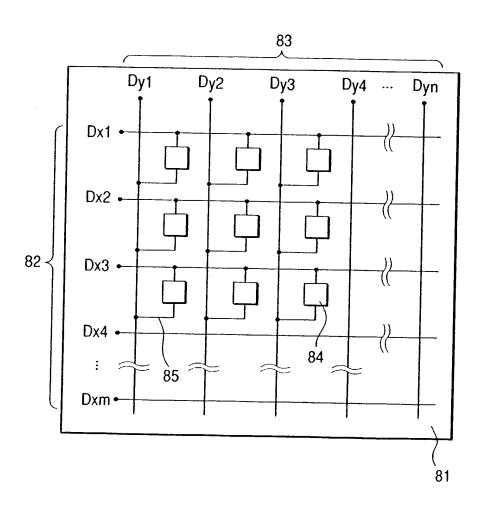


FIG. 8



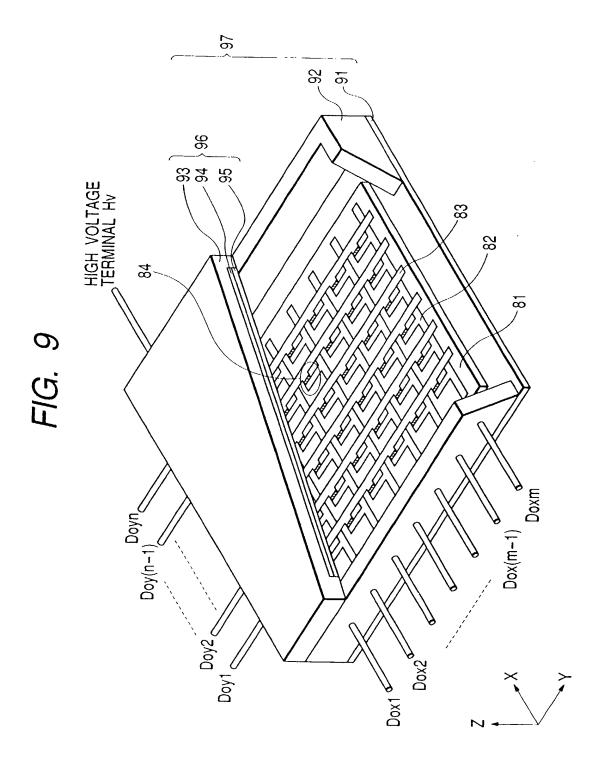


FIG. 10

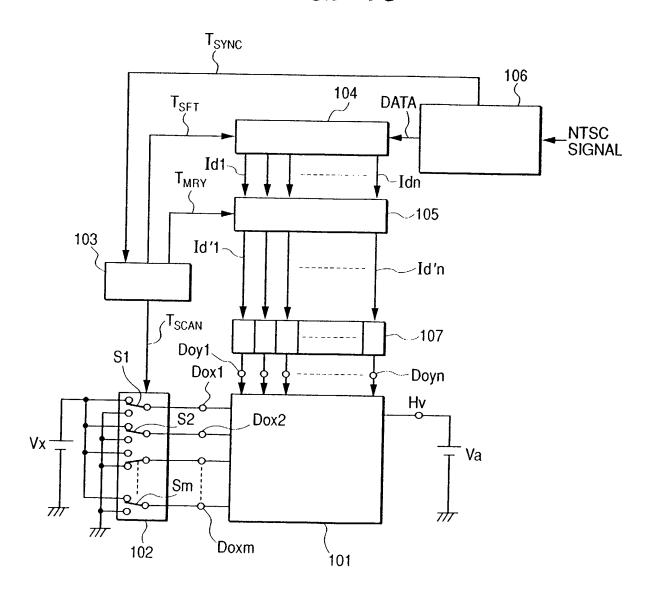


FIG. 11

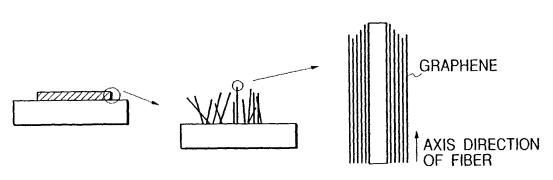


FIG. 12

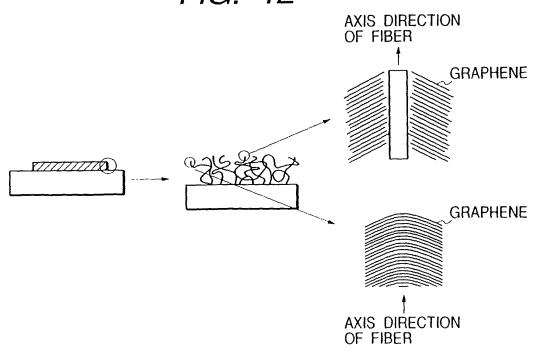


FIG. 13

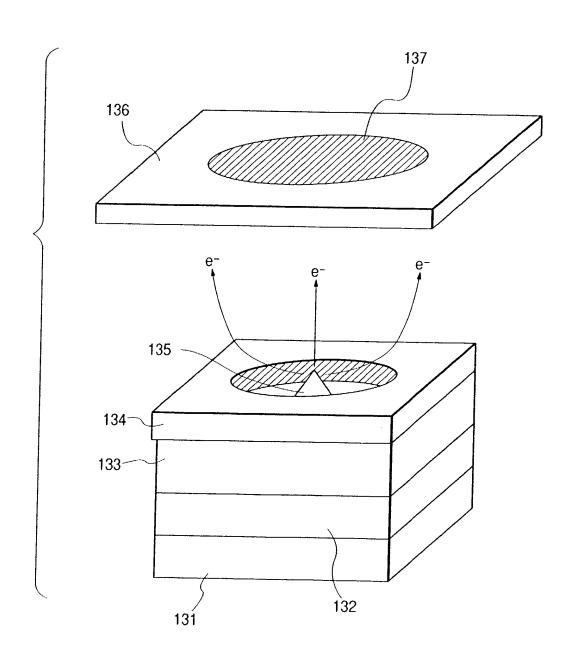
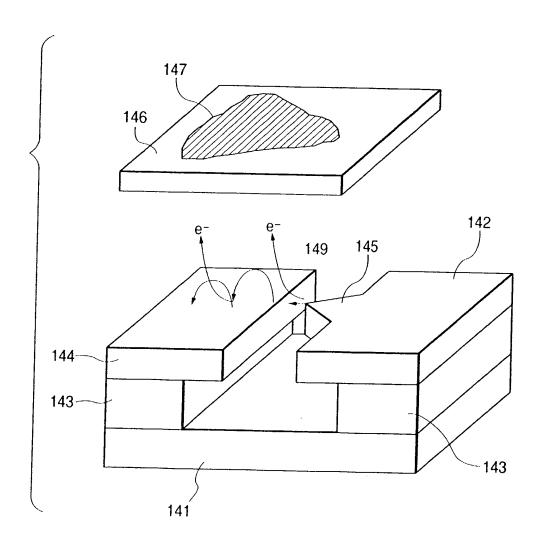


FIG. 14



NOV 3 0 2001 STEELS OF TRACES. RATE

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D/F -8-29-0/

ELECTRON-EMITTING DEVICES, ELECTRON SOURCES, GAU 2879 AND IMAGE-FORMING APPARATUS

BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to electron-emitting devices for emission of electrons, electron sources using them, and image-forming apparatus using the electron sources. The image-forming apparatus according to the present invention can be used in display devices for television broadcasting and the like, display devices of video conference systems, computers, etc., optical printers constructed with use of a photosensitive drum or the like, and so on.

15 Related Background Art

Conventionally, field emission type (FE type)
electron-emitting devices configured to apply a strong
electric field of not less than 10⁶ V/cm to metal and
thereby emit electrons from the metal surface are
drawing attention as one of cold electron sources.

If such FE type cold electron sources become practically available, it will become feasible to construct low-profile emissive type image display devices and they will also contribute to reduction in power consumption and reduction in weight.

Known as an example of a vertical FE type is a device in which, as shown in Fig. 13, an emitter 135 is

of the shape of a circular cone or a quadrangular pyramid formed from a substrate 131 approximately in the vertical direction; for example, one disclosed in C. A. Spindt, "Physical Properties of thin-film field emission cathodes with molybdenum cones," J. Appl. Phys., 47, 5248 (1976) or the like (hereinafter referred to as a Spindt type).

On the other hand, a lateral FE structure is shown in Fig. 14. In the figure, numeral 141 designates a substrate, 142 an emitter electrode, 143 an insulating layer, 145 an emitter, 146 an anode, and 147 a profile of an electron beam irradiating the anode. The emitter 145 sharp-pointed at the tip is arranged in parallel with a gate electrode 144 for extracting electrons from the emitter tip, on the substrate and the collector (anode electrode) is disposed above the substrate on which the gate electrode and the emitter electrode are placed (see USP No. 4,728,851, USP No. 4,904,895, and so on).

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As an example of the electron-emitting devices using fibrous carbon, Japanese Patent Application Laid-Open No. 8-115652 discloses a configuration in which thermal decomposition is implemented in the presence of organic compound gas on fine particles of catalyst metal whereby fibrous carbon is deposited in a fine gap.

As electroconductive layers for carbon nanotubes,

Japanese Patent Application Laid-Open No. 11-194134 and European Patent EP0913508A2 describe metal layers of titanium (Ti), zirconium (Zr), niobium (Nb), tantalum (Ta), and molybdenum (Mo). Japanese Patent Application Laid-Open No. 11-139815 describes Si as an electroconductive substrate.

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The beam profiles of the electron-emitting devices according to the prior arts will be described referring to Figs. 13 and 14.

In Fig. 13, which shows the Spindt type electronemitting device according to the foregoing prior art,
numeral 131 denotes the substrate, 132 the emitter
electrode, 133 the insulating layer, 134 the gate, and
135 the emitter connected to the emitter electrode 132.

When Vf is placed between the emitter 135 and the gate
134, the electric field becomes stronger at the tip of
the projection of the emitter 135 and then electrons
are emitted from the vicinity of the tip of the cone
into the vacuum.

Since the electric field at the tip of the emitter is formed in such a certain finite area as to follow the shape of the emitter tip, the extracted electrons are drawn in the vertical direction relative to the potential from the finite area at the emitter tip.

25 At this time, electrons are also emitted at various angles. As a result, electrons with large angle components are drawn in directions toward the

internal peripheral surface in the hole formed in the gate 134.

As a consequence, where the hole is circular, an electron distribution obtained on the anode 136 in the figure becomes a substantially circular beam profile 137. This indicates that the resultant beam profile is in close relation with the shape of the gate and the distance to the emitter.

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The lateral FE configuration as shown in Fig. 14 is the prior art in which electrons are emitted in the aligned extraction direction.

In Fig. 14, numeral 141 designates the substrate, 142 the emitter electrode, 143 the insulating layer, 144 the gate, and 145 the emitter, and the anode 146 is provided on a substrate opposed to the substrate on which the emitter and gate are disposed.

In the case of the lateral FE configuration constructed in this way, some of electrons emitted from the emitter 145 are extracted (or emitted) into the vacuum, but the rest are taken into the gate 144.

In the configuration shown in Fig. 14, the direction of the electric field vector for emission of electrons (the electric field from the emitter 145 toward the gate 144) is different from the direction of the electric field vector toward the anode 146. As a result, the electron distribution (electron beam spot) becomes large.

SUMMARY OF THE INVENTION

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The prior arts as described above had the following problems.

Since in the foregoing Spindt type the gate and the substrate were constructed in the layered structure, a large gate capacitance and a lot of parasitic capacitances to the emitter were made.

Further, the driving voltage was as high as several ten volts, and there was the drawback of large capacitive power consumption because of the configuration. The Spindt type configuration also had the problem that the beam profile became expanded at the positive electrode (anode).

The foregoing lateral FE configuration had the advantage of capability of reducing the capacitance of the device but had the disadvantage of increasing the driving voltage, because the large distance between the emitter and the gate required several hundred volts for driving. This configuration also had the problem that the beam profile was expanded at the positive electrode (anode).

It is also conceivable to provide the above Spindt type and lateral FE type electron-emitting devices with a beam focusing means, but this raises problems of complexity in a fabrication method, increase in the device area, decrease in electron emission efficiency, and so on.

The present invention has been accomplished in order to solve the above problems and an object of the invention is to provide electron-emitting devices that are reduced in the device capacitance and the driving voltage and improved in the electron emission efficiency and that can provide a high-definition beam stably over a long period, and electron sources and image-forming apparatus using them.

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In order to achieve the above object, an electronemitting device according to the present invention
comprises a first electrode and a second electrode
arranged in opposition to each other with a gap between
first and second electrodes on a surface of a
substrate, and a plurality of fibers electrically
connected to the first electrode and comprising carbon
as a main component, and the fibers are placed on a
surface of the first electrode facing the second
electrode.

In order to achieve the above object, another electron-emitting device according to the present invention comprises an extraction electrode and a cathode electrode formed in opposition to each other with a gap between the extraction electrode and the negative electrode on an electrically insulating substrate, a first layer formed on the negative electrode and having an oxide of Ti, an oxide of Zr, or an oxide of Nb on a surface thereof, and a fibrous

carbon grown through a catalyst particle disposed on a side wall surface of the first layer on the extraction electrode side.

An electron source according to the present invention is characterized by a plurality of above-stated electron-emitting devices arrayed.

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An image-forming apparatus according to the present invention is characterized by use of the above electron source.

10 According to the present invention, it is feasible to provide the electron-emitting devices presenting a small electron beam spot on the anode, achieving excellent electron emission efficiency, and having excellent durability, a small capacitance component, and excellent stability. The electron sources using the electron-emitting devices can realize quick responsivity and low power consumption. The image-forming apparatus using the electron sources can provide high-definition images with high luminance over a long period, in addition to the quick responsivity and low power consumption.

BRIEF DESCRIPTION OF THE DRAWINGS

Figs. 1A and 1B are schematic views showing an electron-emitting device according to an embodiment and Example 1 of the present invention;

Figs. 2A and 2B are schematic views showing

another electron-emitting device according to Example 2 of the present invention;

Figs. 3A and 3B are schematic views showing still another electron-emitting device according to Example 3 of the present invention;

Figs. 4A and 4B are schematic views showing still another electron-emitting device according to Example 4 of the present invention;

Figs. 5A, 5B, 5C, 5D and 5E are step diagrams for production of the electron-emitting device according to Example 1 of the present invention;

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Fig. 6 is a diagram for explaining the operation of the electron-emitting device;

Fig. 7 is a characteristic diagram of the fundamental operation of the electron-emitting device;

Fig. 8 is a schematic plan view of an electron source according to an embodiment of the present invention;

Fig. 9 is a perspective view of an image-forming
apparatus, partly broken, according to an embodiment of
the present invention;

Fig. 10 is a block diagram of an image-forming apparatus according to an embodiment of the present invention;

25 Fig. 11 is a schematic structure diagram of fibrous carbons (carbon nanotubes);

Fig. 12 is a schematic structure diagram of

fibrous carbons (graphite nanofibers);

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Fig. 13 is a schematic structure diagram of the vertical FE configuration according to the prior art; and

5 Fig. 14 is a schematic structure diagram of the lateral FE configuration according to the prior art.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The embodiments of the present invention will be illustratively described hereinafter in detail with reference to the drawings. It is, however, noted that, as to the dimensions, materials, shapes, relative locations, etc. of the components described in the embodiments, the scope of the invention is by no means intended to be limited only to those unless otherwise stated specifically.

The inventors conducted research on materials that permitted fine (several nm order) nuclei (catalyst particles) to be formed thereon from a catalyst and that formed stable electrical coupling with fibrous carbons grown from the nuclei by thermal decomposition.

From the research, the inventor found that preferable materials permitting the growth of the fibrous carbons through the catalyst and achieving electrical coupling therewith were materials selected from Ti, Zr, and Nb and oxidized in part (at the interface in contact with the fibrous carbons or the

catalyst), or oxide semiconductors of materials selected from Ti, Zr, and Nb.

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From detailed investigation, the inventor further found that the fibrous carbons were able to be produced at the position of the catalyst particles with good repeatability, by use of a member in which the catalyst particles (particularly preferably, Pd particles) were placed on an oxide of a material selected from Ti, Zr, and Nb.

In tandem with it, the inventor also found that materials on which no fibrous carbon grew or on which a growth rate of fibrous carbon was low, were Ta, Cr, Au, Ag, Pt, and materials of the same kinds as the catalyst materials.

The growth of the fibrous carbons over these materials is also valid in the layered structure. For example, Cr was deposited over the entire surface of a substrate, a fine region of titanium oxide was further formed on the Cr layer, and the entire surface of the substrate was coated with palladium oxide. With use of this substrate, the fibrous carbons were selectively grown only above titanium oxide.

Then the electron-emitting devices, electron sources, and image-forming apparatus using the fibrous carbons according to the present invention, using the technology of forming the fibrous carbons at a desired position with good repeatability as described above,

will be described below in comparison with the prior art examples.

First, the inventors also conducted research about a method of forming a high-definition electron beam.

The high-definition beam forming method will be described below.

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In general, the operating voltage Vf of the FE device is determined by the electric field at the tip portion of the emitter, which is derived by the Poisson's equation, and the current density of electron emission current obtained according to a relation called the Fowler-Nordheim equation, using the electric field and a work function at the emitter portion as parameters.

As for the electric field necessary for the electron emission, the smaller the distance d between the emitter tip and the gate electrode, or the smaller the radius r of the emitter tip, the stronger the electric field is established.

On the other hand, the maximum X-directional size Xd of the electron beam on the anode (for example, the maximum range from the center of the circular beam profile 137 in Fig. 13) is expressed in the form proportional to $\sqrt{(Vf/Va)}$ in simple computation.

As apparent from this relation, increase in Vf results in increase in the beam size.

From this consideration, the distance d and radius

r need to be set as small as possible in order to decrease Vf.

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The beam profiles of the conventional configurations will be described below using Figs. 13 and 14. In the figures, numerals common thereto denote as follows: 131, 141 the substrate; 132, 142 the emitter electrode; 133, 143 the insulating layer; 135, 145 the emitter; 136, 146 the anode; 137, 147 the shape of the electron beam irradiating the anode.

In the case of the foregoing Spindt type, as shown in Fig. 13, when Vf is applied between the emitter 135 and the gate 134, the electric field becomes stronger at the tip of the projection of the emitter 135, and electrons are taken out from near the tip of the conical emitter into the vacuum.

Since the electric field at the tip of the emitter 135 is formed in such a certain finite area as to follow the shape of the tip of the emitter 135, electrons extracted are drawn in the vertical direction relative to the potential from the finite area of the tip of the emitter 135.

At this time, electrons are emitted at various angles and electrons with large angle components are drawn in directions toward the gate. When the gate 134 is circular, the electron distribution on the anode 136 becomes the substantially circular beam profile 137 as shown in the figure.

Namely, the resultant beam profile is in close relation with the shape of the extraction gate and the distance to the emitter.

In the case of the lateral FE configuration (Fig. 14) wherein electrons are extracted in the aligned extraction direction, the very strong electric field (lateral electric field) is created substantially in parallel to the surface of the substrate 141 between the emitter 145 and the gate 144, so that among electrons emitted from the emitter 145, some electrons 149 are drawn into the vacuum and the remaining electrons are taken into the gate electrode 144.

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In the case of the configuration shown in this
Fig. 14, the direction of the electric field vector for
the emission of electrons (the electric field directed
from the emitter 145 toward the gate 144) is different
from the direction of the electric field vector
directed toward the anode (anode electrode) 146. For
this reason, the emitted electrons form a large
electron distribution (beam spot) on the anode 146.

Here let us further consider the electric field for extracting electrons from the emitter electrode 145 (which will be called a "lateral electric field" herein for convenience' sake and the enhancement effect of the electric field by the emitter shape will be ignored herein) and the electric field directed toward the anode (which will be called a "vertical electric field"

herein).

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In the configurations of Fig. 13 and Fig. 14, the foregoing "lateral electric field" can also be referred to as an "electric field in the substantially parallel direction to the surface of the substrate 131 (141)". Particularly, in the configuration of Fig. 14, it can also be referred to as an "electric field in the facing direction of the gate 144 and the emitter 145".

In the configurations of Fig. 13 and Fig. 14, the foregoing "vertical electric field" can also be referred to as an "electric field in the substantially normal direction to the surface of the substrate 131 (141)" or as an "electric field in the facing direction of the substrate 131 (141) and the anode 136 (146)".

As described previously, electrons emitted from the emitter 145 are first drawn by the lateral electric field to fly toward the gate 144 and thereafter they are moved up by the vertical electric field to reach the anode 146.

Important points at this time are a ratio of strengths of the lateral electric field and the vertical electric field and the relative position of electron emission point.

When the lateral electric field is stronger in order of magnitude than the vertical electric field, most of the electrons emitted from the emitter fly in trajectories gradually bent by radial potentials formed

by the lateral electric field and directed toward the gate. Part of the electrons colliding with the gate are again emitted because of scattering, and thereafter are repeatedly scattered as spreading on the gate while drawing trajectories similar to ellipses many times and as reducing the number of emitted electrons, before they are captured by the vertical electric field. When the scattered electrons then cross an equipotential line made by the gate potential (which is also called a "stagnation point"), they are moved up by the vertical electric field for the first time.

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When the lateral electric field and the vertical electric field are approximately equal in strength to each other, the extracted electrons also fly in trajectories bent by the radial potentials, but the binding by the electric field becomes weaker, so that there appear trajectories of electrons captured by the vertical electric field without colliding with the gate 144.

It was verified that with the lateral electric field and vertical electric field approximately equal in strength to each other, as the position of the electron emission point from the emitter 145 was gradually lifted up from the plane to which the gate

144 belonged, toward the plane to which the anode 146 belonged (see Fig. 6), the emitted electrons could fly in trajectories captured by the vertical electric field

without colliding with the gate 144 at all.

Research was conducted about the electric field ratios and it was found from the research that, where d represented the spacing between the gate electrode 144 and the tip of the emitter electrode 145, V1 the potential difference (the potential difference between the gate electrode and the emitter electrode) during driving of the device, H the distance between the positive electrode (anode) and the substrate (device), and V2 (Va) the potential difference between the positive electrode (anode) and the negative electrode (emitter electrode), the extracted electrons drew the trajectories colliding with the gate when the lateral electric field was 50 or more times stronger than the vertical electric field.

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The inventor also discovered that there existed a height's causing no substantial scattering on the gate electrode 2 (which is defined by a distance between a plane including part of the surface of the gate electrode 2 and being substantially parallel to the surface of the substrate 1 and a plane including the surface of the electron-emitting member 4 and being substantially parallel to the surface of the substrate 1 (see Fig. 6)). This height is dependent upon the ratio of the vertical electric field and the lateral electric field (strength of the vertical electric field) and the

height becomes lower with decrease in the verticallateral electric field ratio and becomes higher with increase in the lateral electric field.

A practical fabrication range of the height s is not less than 10 nm nor more than 10 μm .

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In the conventional configuration shown in Fig. 14, since the gate 144 and the emitter (142, 145) were formed at the same height on the same plane and since the lateral electric field was stronger by one or more figures than the vertical electric field, there was the strong tendency that the number of extracted electrons into the vacuum decreased because of the collision with the gate.

Further, in the conventional configuration, since the thickness and width of the gate electrode and the relative positions of the gate, emitter, and anode were determined for the purpose of enhancing the intensity of the lateral electric field, the electron distribution on the anode became expanded.

As described previously, in order to make small the distribution of electrons reaching the anode 146, it is necessary to consider 1) decreasing the driving voltage (Vf), 2) aligning the extraction directions of electrons, 3) trajectories of electrons, and, further, in the case involving the scattering on the gate, 4) the scattering mechanisms of electrons (particularly, elastic scattering).

The electron-emitting devices using the fibrous carbons according to the present invention realize both the size reduction of the electron distribution on the anode electrode and improvement in the electron emission efficiency (decrease of emitted electrons absorbed by the gate electrode).

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Configurations of the electron-emitting devices according to the present invention will be described below in further detail with reference to the drawings. Figs. 1A and 1B are schematic views showing an example of the electron-emitting device according to the present invention, wherein Fig. 1A is a plan view thereof and Fig. 1B a cross-sectional view along 1B-1B in Fig. 1A. Fig. 6 is a schematic cross-sectional view showing a state of driving of the electron-emitting apparatus according to the present invention in which the anode electrode is placed above the electron-emitting device of the present invention.

In Figs. 1A and 1B and Fig. 6, numeral 1
designates an electrically insulating substrate, 2 an
extraction electrode (also called "gate electrode" or
"second electrode"), 3 a negative electrode (also
called "first electrode" or "cathode electrode"), 4
fibrous carbons being an emitter material (also called
"electron-emitting material" or "electron-emitting
member"), and 5 a first layer for selective growth of
the fibrous carbons, which is an oxide of a material

selected from Ti, Zr, and Nb, described previously.

The fibrous carbons constituting the electron-emitting material 4 are electrically connected to the electrode

3. Numeral 6 denotes a second layer.

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In the present invention, the important structure is that the negative electrode 3 and the extraction electrode 2 are placed with a gap in between on the surface of the substrate and a plurality of fibrous carbons 4 are placed on a surface of the negative electrode 3 facing the extraction electrode 2. In other words, the plurality of fibrous carbons extending in the facing direction of the negative electrode 3 and the extraction electrode 2 are located on the negative electrode 3 in the gap between the negative electrode 3 and the extraction electrode 2. This configuration permits electrons to be emitted by a lower electric field.

Further, in the present invention, the important structure is that, in order to prevent unnecessary electrons from being emitted, the fibrous carbons are not placed on the surfaces except for the surface facing the extraction electrode 2. This structure can restrain the expansion of the electron beam irradiating the anode electrode.

In the example of Figs. 1A, 1B, the first layer 5 and the second layer 6 are provided for controlling the region where the fibrous carbons are formed. Namely,

the first layer 5 is made of a material permitting the fibrous carbons 4 to grow thereon, while the second layer 6 is made of a material not permitting the fibrous carbons 4 to grow thereon, as compared with the 5 first layer 5. The first layer and second layer described above are preferably electrically conductive. Particularly, the second layer is especially preferably electrically conductive, because it is exposed in In the configuration as shown in Figs. 1A, 1B, 10 unless the first layer 5 is electrically conductive, electrical connection cannot be established between the negative electrode 3 and the fibrous carbons; therefore, the first layer 5 is preferably selected from electroconductive materials.

The example with provision of the second layer 6
was described herein, but this layer does not always
have to be provided. For example, it is also possible
to construct an electron-emitting device of the present
invention by making the negative electrode 3 of a

material selected from Ti, Zr, and Nb and oxidizing
only a surface thereof facing the extraction electrode
among its surfaces (i.e., by placing the first
layer).

In the form shown in Figs. 1A, 1B, all the first layer 5 does not have to be made of an oxide, but it is also possible to make at least only the surface facing to the extraction electrode 2 among the surfaces of the

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first layer 5, of an oxide. This structure makes the second layer not always necessary. Even if the first layer is thick, such structure can enhance the electrical connection between the negative electrode 3 and the fibrous carbons.

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The electron-emitting device according to the present invention can also be constructed in such a way that the negative electrode 3 is made of a material selected from Ti, Zr, and Nb, the surface thereof (including the surface facing the extraction electrode 2) is oxidized, and the surfaces other than the surface facing the extraction electrode 2 (i.e., the surface on which the fibrous carbons are laid) are coated with a layer (the second layer) made of a material permitting no growth of fibrous carbons as compared with the oxide of the material selected from Ti, Zr, and Nb.

In the electron-emitting apparatus of the present invention, as shown in Figs. 1A, 1B and Fig. 6, the plane including the surface of the electron-emitting member 4 and being substantially parallel to the surface of the substrate 1 is preferably more distant from the surface of the substrate than the plane including part of the surface of the gate electrode 2 and being substantially parallel to the surface of the substrate 1. In other words, in the electron-emitting apparatus of the present invention, the plane including part of the surface of the electron-emitting member 4

and being substantially parallel to the surface of the substrate 1 is located between the anode electrode 61 and the plane including part of the surface of the extraction electrode 2 and being substantially parallel to the surface of the substrate. This structure can realize the reduction of electrons absorbed into the gate electrode and the reduction of the spot size of the electron beam impinging on the anode electrode.

Further, in the electron-emitting device of the present invention, the electron-emitting member 4 is located at the height s (defined as the distance between the plane including part of the surface of the gate electrode 2 and being substantially parallel to the surface of the substrate 1 and the plane including the surface of the electron-emitting member 4 and being substantially parallel to the surface of the substrate 1) at which no substantial scattering of electrons occurs on the gate electrode 2.

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The above height s is dependent upon the ratio of

the vertical electric field and the lateral electric

field (intensity of the vertical electric

field/intensity of the lateral electric field), and the

height needs to be decreased with decrease in the ratio

of the vertical electric field and the lateral electric

field and to be increased with increase in the

intensity of the lateral electric field; the practical

range of the height s is not less than 10 nm nor more

than 10 pm.

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This structure can be readily realized, for example, by making the thickness of the negative electrode 3 larger than the thickness of the extraction electrode 2. Alternatively, it can also be realized by forming the negative electrode 3 and the extraction electrode 2 in equivalent thickness and placing the first layer 5 on the negative electrode 3.

In the electron-emitting apparatus of the present invention, where, in the structure shown in Fig. 6, d represents the distance of the gap between the negative electrode 3 and the gate electrode 2, Vf the potential difference during driving of the electron-emitting device (the voltage between the negative electrode 3 and the gate electrode 2), H the distance between the anode electrode 61 and the surface of the substrate 1 on which the device is placed, and Va the potential difference between the anode electrode 61 and the negative electrode 3, the electric field (lateral electric field) during the driving: E1 = Vf/d is set to be not less than 1 times nor more than 50 times stronger than the electric field (vertical electric field) between the anode 61 and the cathode 3: E2 = Va/H.

This setting can almost nullify the ratio of electrons colliding with the gate electrode 2 to electrons emitted from the negative electrode 3. As a

result, there are provided the electron-emitting device and the electron-emitting apparatus with the extremely small spread of the emitted electron beam and with high electron emission efficiency.

The "lateral electric field" stated in the present invention can be referred to as the "electric field in the direction substantially parallel to the surface of the substrate 1". In another sense, it can also be referred to as the "electric field in the facing direction of the gate 2 and the cathode electrode 3". The "vertical electric field" stated in the present invention can be referred to as the "electric field in the direction substantially normal to the surface of the substrate 1" or the "electric field in the facing direction of the substrate 1 and the anode electrode 61".

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The electrically insulating substrate 1 can be either of laminations in which SiO, is laid by sputtering or the like on a well-cleaned surface of either of silica glass, glasses partly replaced with K or the like while reducing the impurity content of Na and others, soda lime glass, silicon substrates, etc. insulating substrates of ceramics such as alumina or the like, and so on.

25 The extraction electrode 2 and the negative electrode 3 are electrically conductive and are made by either of the ordinary vacuum film-forming technologies

such as vacuum evaporation, sputtering, and the like, or the photolithography technology.

The materials of the extraction electrode 2 and the negative electrode 3 are adequately selected, for example, from carbon, metals, nitrides of metals, carbides of metals, borides of metals, semiconductors, and metal semiconductors coumpounds.

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The thicknesses of the extraction electrode 2 and the negative electrode 3 are set in the range of several ten nm to several ten pm. Preferably, they are desirably made of either of heat resistant materials such as carbon, metals, nitrides of metals, and carbides of metals.

When there is a worry that a potential drop or the like can occur because of the small thickness of the electrodes or when such devices are used in a matrix array, a low-resistant metal material for wiring is sometimes used in portions not associated with the emission of electrons as occasion may demand.

In comparison of electric field intensities between the electron emission field of the cathode material used (the lateral electric field) and the vertical electric field necessary for the formation of image, the gap between the extraction electrode 2 and the negative electrode 3 (the width of the gap) and the driving voltage are preferably designed so that the electron emission field becomes approximately 1 times

to 50 times stronger than the vertical electric field.

In the present invention, the emitter (electronemitting member) 4 is comprised of fibrous carbons.

The fibrous carbons are preferably those obtained by forming nuclei with use of a catalyst and growing the fibrous carbons from the nuclei by thermal decomposition.

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According to the present invention, the "fibrous carbons" can also be said as "columnar substances comprising carbon as a main component" or "linear substances comprising carbon as a main component". The "fibrous carbons" can also be mentioned as "fibers comprising carbon as a main component". More specifically, the "fibrous carbons" in the present invention embrace carbon nanotubes, graphite nanofibers, and amorphous carbon fibers. Among these, the graphite nanofibers are most preferable for the electron-emitting member 4.

negative electrode 3 and the driving voltage are preferably designed so that, in comparison of electric field intensities between the electron emission field of the electron-emitting member (the lateral electric field) and the vertical electric field necessary for the formation of image, the electron emission field becomes approximately 1 times to 50 times stronger than the vertical electric field, as described previously.

When a light emitting member such as a phosphor or the like is placed on the positive electrode (anode electrode), the necessary vertical field is preferably in the range of not less than 10⁻¹ V/pm nor more than 10 V/pm. For example, where the gap between the positive electrode (anode electrode) and the negative electrode is 2 mm and 10 kV is placed in the gap, the vertical electric field at this time is 5 V/pm. In this case, the emitter material (electron-emitting member) 4 to be used is one having the electron emission field larger than 5 V/pm, and the spacing and driving voltage can be determined so as to realize the selected electron emission field.

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The aforementioned fibrous carbons are preferably applicable as materials having the threshold electric field of several V/µm as described above.

Fig. 11 and Fig. 12 show examples of forms of the fibrous carbons suitably applicable to the present invention. In each figure the left view schematically shows a form observed at the optical microscope level (approximately 1000×), the center view a form observed at the scanning electron microscope (SEM) level (approximately 30,000×), and the right view a form of carbon observed at the transmission electron microscope (TEM) level (approximately 1 million×).

As shown in Fig. 11, the form of cylindrical shape of graphen is called a carbon nanotube (a multiple

structure of cylinders is called a multiwall nanotube), and the threshold thereof becomes the lowest, particularly, in the structure in which the tube is open at the tip.

5 As another example, fibrous carbons may be produced at relatively low temperatures are shown in Fig. 12. A fibrous carbon of this form is comprised of a lamination of graphens (which is thus sometimes called "graphite nanofiber" and the rate of amorphous 10 structure of which increases depending upon the temperature). More specifically, the graphite nanofiber indicates a fibrous substance in which graphens are layered (laminated) in the longitudinal direction thereof (in the axis direction of the fiber). 15 In other words, as shown in Fig. 12, it is a fibrous substance in which a plurality of graphens are arranged and layered (laminated) so as not to be parallel to the axis of fiber.

On the other hand, a carbon nanotube is a fibrous substance in which graphens are arranged (in cylindrical shape) around the longitudinal direction (the axis direction of fiber). In other words, it is a fibrous substance in which graphens are arranged substantially in parallel to the axis of the fiber.

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A single surface of graphite will be called a "graphen" or "graphen sheet". More specifically, graphite is a lamination in which carbon planes, each

of which is a spread of regular hexagons consisting of covalent bonds of carbon atoms in sp2 hybrid, are layered at intervals of distance of 3.354 Å. Each of the carbon planes is called a "graphen" or "graphen sheet".

All the fibrous carbons have the threshold for the emission of electron in the range of approximately 1 to 10 V/ μm and are very suitable for the emitter (electron-emitting member) 4 of the present invention.

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Particularly, the electron-emitting devices using the graphite nanofibers can be those capable of emitting electrons at a low electric field and yielding a large emission current, capable of being produced readily, and exhibiting stable electron emission 15 characteristics, without having to be limited to the device structure of the present invention shown in Figs. 1A, 1B and others. For example, an electronemitting device can be constructed by making the emitter of graphite nanofibers and preparing the electrode for control of electron emission from this emitter, and a light emitting apparatus such as a lamp or the like can also be formed by using a light emitting member which emits light under irradiation of electrons emitted from the graphite nanofibers.

25 Further, it is also possible to construct an image display apparatus such as a display or the like by arraying a plurality of such electron-emitting devices using the graphite nanofibers and preparing an anode electrode having a light emitting member such as a phosphor or the like. In the electron-emitting apparatus, the light emitting apparatus, and the image display apparatus using the graphite nanofibers, stable electron emission can be implemented without need for maintaining the interior in such an ultrahigh vacuum as required in the conventional electron-emitting devices, and a high electron emission amount can be ensured at a low electric field; therefore, the apparatus can be fabricated extremely simply with high reliability.

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The aforementioned fibrous carbons can be made by decomposing a hydrocarbon gas under use of a catalyst (a material for promoting deposition of carbon). The carbon nanotubes and graphite nanofibers differ depending upon the type of the catalyst and the temperature of decomposition.

The catalyst materials, such as Fe, Co, Pd, Ni and alloy of material selected from those materials can be used as the nuclei for formation of the fibrous carbons.

Particularly, in the case of Pd, the graphite nanofibers can be produced at low temperatures (temperatures of not less than 400°C). On the other hand, when the catalyst is Fe or Co, the temperature for production of carbon nanotubes needs to be not less than 800°C. Since the production of the graphite

nanofiber material using Pd can be implemented at low temperatures, it is also preferable in terms of influence on the other members and the production cost.

Further, in the case of the Pd catalyst, using the property that the oxide thereof is readily reduced by hydrogen at low temperatures (room temperature), it is feasible to use palladium oxide as a nucleation material.

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By employing the hydrogen reduction treatment of palladium oxide, it became feasible to form the initial aggregated nuclei at relatively low temperatures (200°C or less) without use of thermal aggregation of metal thin film or production and evaporation of ultrafine particles accompanied by a danger of explosion which are conventionally used as ordinary nucleation techniques.

The foregoing hydrocarbon gas can be, for example, either of hydrocarbon gases such as ethylene, methane, propane, propylene, and so on, or vapors of organic solvents such as ethanol, acetone, and so on.

The raw materials for the fibrous carbons can also be such raw materials as ${\rm CO}$, ${\rm CO}_2$, and the like, in addition to the foregoing hydrocarbon gases.

The material of the layer 5 allowing the growth of fibrous carbons 4 is a mixture of Ti and an oxide thereof resulting from partial oxidation of Ti, or an oxide semiconductor of Ti; or a mixture of Zr and an

oxide thereof resulting from partial oxidation of Zr, or an oxide semiconductor of Zr; or a mixture of Nb and an oxide thereof resulting from partial oxidation of Nb, or an oxide semiconductor of Nb, as described previously. The foregoing oxide of Ti, oxide of Zr, or oxide of Nb is placed at least on the surface for the fibrous carbons 4 to be placed, among the surfaces of the layer 5.

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These oxides of Ti, Zr, and Nb are stoichiometrically insulators, but weakly oxidized substances thereof or suboxides thereof possess a number of defects inside and thus form semiconductors of the oxygen deficient type or the like.

The layer 5 and the catalyst particles placed on the layer 5 can be produced, for example, by a method of baking Pd on the layer of Ti, Zr, or Nb at the temperature of about 300°C for about several ten minutes to form palladium oxide and simultaneously oxidizing the layer of Ti, Zr, or Nb as well. The baking temperature and time of this level, however, do not oxidize the entire layer, though depending upon the thickness of the layer of Ti, Zr, or Nb, but oxidize only the surface. Since such oxide has the semiconductorlike nature as described above, the layer 5 thus formed results in possessing electrical conductivity.

The second layer 6 is comprised of a material on

which no substantial growth of fibrous carbon occurs, as compared with the first layer 5, even if the catalyst particles are placed thereon. Such materials can be aforementioned Ta, Cr, Au, Ag, Pt, or materials of the same kinds as the catalyst materials. Then the region except for the side face of the first layer 5 on the extraction electrode 2 side is covered by the second layer 6.

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As a result, only the side wall of the layer 5 on the extraction electrode 2 side is exposed, and thus the fibrous carbons 4 grow only on the side wall on the extraction electrode 2 side in the subsequent step of growth of fibrous carbons.

If the device should not have the conductive layer 6 on which the fibrous carbons do not grow through the fine catalyst particles, the fibrous carbons would grow over the entire surface of the conductive layer 5 on which the fibrous carbons can grow through the fine catalyst particles. In this case, the fibrous carbons apart from the gate electrode 2 would be involved in emission of electrons, though it is a little, and such electrons could disturb the beam profile and uniformity.

In contrast with it, the electron-emitting device according to the present embodiment can be constructed in the configuration wherein there exists no fibrous carbons on the side walls except for the side wall on

the extraction electrode 2 side, and it is thus feasible to prevent the disturbance of the beam profile and uniformity.

The position of the electron emission point in the emitter region and the operation thereof will be described below referring to Fig. 6 and Fig. 7.

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The instant device having the gap length d of several µm was placed in a vacuum chamber 60, as shown in Fig. 6, and then the interior thereof was evacuated well down to about 10⁻⁴ Pa by an vacuum pump 65. While the positive electrode (hereinafter referred to as an anode) 61 was set at the position of the height H of several millimeters from the substrate 1, a high voltage Va of several kV was applied from a voltage source.

A fluorescent member 62 with an electroconductive film coating thereon was placed on the anode 61.

A pulse voltage of about several ten V was applied as the driving voltage Vf between the electrode 2 and the electrode 3 to measure the device current If and electron emission current Ie. Naturally, the driving voltage Vf was applied so that the potential at the gate electrode 2 was higher than that at the negative electrode 3.

At this time, equipotential lines 63 are formed as shown, and the electric field is most concentrated at the part indicated by point 64 closest to the anode 61

among the fibrous carbons 4 of the electron-emitting material and inside the gap.

It is speculated that electrons are emitted from the site where the electric field is most concentrated in the electron-emitting material located in the vicinity of this field concentrating point 64.

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The Ie characteristic of the device was that shown in Fig. 7. Namely, Ie demonstrated a sudden rise from about half of the applied voltage, and If, not shown, was similar to the characteristic of Ie but considerably smaller than Ie.

Based on this principle, an electron source and an image-forming apparatus comprised of a plurality of electron-emitting devices according to the embodiment of the present invention will be described hereinafter with reference to Fig. 8 to Fig. 10. Fig. 8 is a schematic plan view of electron source according to an embodiment of the present invention, Fig. 9 a perspective view of an image-forming apparatus, partly broken, according to an embodiment of the present invention, and Fig. 10 a block diagram of an image-forming apparatus according to an embodiment of the present invention.

In Fig. 8, numeral 81 denotes an electron source substrate, 82 X-directional wires, and 83 Y-directional wires. Numeral 84 denotes electron-emitting devices according to the embodiment of the present invention,

and 85 interconnections.

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In this configuration the placement of plural electron-emitting devices 84 is accompanied by increase in the capacitance of the devices, and there arises a problem that in the matrix wiring shown in Fig. 8, waves become dull because of the capacitance component, so as to fail to attain expected gradation even with application of short pulses according to pulse width modulation.

In order to avoid it, it is preferable to employ a structure for reducing the increase of the capacitance component except for that in the electron emission section, for example, by placing an interlayer electric film (rear plate 91) right next to the electron emission section, as shown in Fig. 9.

In Fig. 8, the m X-directional wires 82 consist of DX_1 , DX_2 ,..., DX_m and are made of an aluminum based wiring material in the thickness of about 1 $\mu\mathrm{m}$ and in the width of 300 $\mu\mathrm{m}$ by evaporation. However, the material, thickness, and width of the wires are properly designed according to respective cases.

On the other hand, the Y-directional wires 83 consist of n wires of DY_1 , DY_2 ,..., DY_n 0.5 µm thick and 100 µm wide and are made in similar fashion to the X-directional wires 82.

An interlayer dielectric film not shown is disposed between these m X-directional wires 82 and n

Y-directional wires 83, so as to electrically isolate them from each other (where m and n are positive integers).

The unrepresented interlayer dielectric film is made of ${\rm SiO}_2$ in the thickness of about 0.8 μm by sputtering or the like.

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The interlayer dielectric film is formed in the desired shape over the entire surface or in part of the substrate 81 after formation of the X-directional wires 82, and the thickness of the interlayer dielectric film is determined so that the device capacitance per device is not more than 1 pF and the device withstand voltage 30 V in the present embodiment, particularly, in order to resist the potential difference at intersections between the X-directional wires 82 and the Y-directional wires 83. The X-directional wires 82 and Y-directional wires 83 are drawn out as respective external terminals.

Pairs of electrodes (not shown) making up the electron-emitting devices 84 according to the embodiment of the present invention are electrically connected by the m X-directional wires 82, n Y-directional wires 83, and interconnections 85 of an electroconductive metal or the like.

Connected to the X-directional wires 82 is an unrepresented scanning signal applying means for applying a scanning signal for selection of a row of

electron-emitting devices 84 according to the embodiment of the present invention, arrayed in the X-direction.

Connected to the Y-directional wires 83 on the other hand is an unrepresented modulation signal generating means for modulating each column of electron-emitting devices 84 according to the embodiment of the present invention, arrayed in the Y-direction, according to an input signal.

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The driving voltage applied to each electronemitting device is supplied as a difference signal
between a scanning signal and a modulation signal
applied to the device. In the embodiment of the
present invention, electrical connection is established
so that the Y-directional wires are at a higher
potential while the X-directional wires at a lower
potential. This connection yields the beam converging
effect, which is a feature of the embodiment of the
present invention.

In the above configuration, the individual devices can be selected to be driven independently by use of the simple matrix wiring.

An image-forming apparatus constructed by use of the electron source of this simple matrix configuration will be described referring to Fig. 9. Fig. 9 shows a display panel of the image-forming apparatus wherein soda lime glass is used as a material of a glass substrate.

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In Fig. 9, numeral 81 designates an electron source substrate loaded with a plurality of electron-emitting devices, 91 a rear plate to which the electron source substrate 81 is fixed, and 96 a face plate wherein a florescent film 94, a metal back 95, etc. are formed on an internal surface of glass substrate 93.

Numeral 92 denotes a support frame, and the rear plate 91 and face plate 96 are coupled to this support frame 92 with frit glass or the like. Numeral 97 represents an envelope which is sealed by baking it in the temperature range of 450°C in vacuum for ten minutes.

Numeral 84 indicates the electron emission regions and numerals 82 and 83 denote the X-directional wires and Y-directional wires, respectively, which are connected to the pairs of device electrodes of the electron-emitting devices according to the embodiment of the present invention.

The envelope 97 is composed of the face plate 96, the support frame 92, and the rear plate 91, as described above. When an unrepresented support called a spacer is interposed between the face plate 96 and the rear plate 91, the envelope 97 can be constructed with sufficient strength against the atmospheric pressure.

The metal back 95 can be made in such a way that after production of the fluorescent film, the internal

surface of the fluorescent film is subjected to a smoothing process (normally called "filming") and thereafter Al is deposited thereon by vacuum evaporation or the like.

The face plate 96 is further provided with a transparent electrode (not shown) on the outer surface side of the fluorescent film 94, in order to further enhance the electrical conductivity of the fluorescent film 94.

During the aforementioned sealing operation, in the color display case, correspondence has to be made between respective color phosphors and electronemitting devices and thus sufficient alignment is essential.

Next, a scanning circuit 102 shown in Fig. 10 will be described below. This circuit is provided with M switching devices inside (schematically indicated by S1 to Sm in the figure). Each switching device selects either an output voltage of a dc voltage source Vx or 0 V (the ground level) to be electrically connected to a terminal Dx1 to Dxm of display panel 101.

Each switching device of S1 to Sm operates based on a control signal Tscan from a control circuit 103 and can be constructed, for example, of a combination of switching devices such as FETs.

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The dc voltage source Vx is set to output such a constant voltage that the driving voltage applied to

non-scanned devices is not more than the electron emission threshold voltage, based on the characteristics of the electron-emitting devices (electron emission threshold voltage) according to the embodiment of the invention, in the case of the present example.

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The control circuit 103 has the function of matching operations of respective portions so as to implement appropriate display based on image signals supplied from the outside. The control circuit 103 generates control signals of Tscan, Tsft, and Tmry to the respective portions, based on a synchronizing signal Tsync supplied from a synchronizing signal separating circuit 106.

The synchronizing circuit 106 is a circuit for separating the synchronizing signal component and luminance signal component from a TV signal of the NTSC system supplied from the outside, and can be composed of an ordinary frequency separating (filter) circuit or the like.

Although the synchronizing signal separated by the synchronizing signal separating circuit 106 consists of a vertical synchronizing signal and a horizontal synchronizing signal, it is illustrated as a Tsync signal herein for convenience' sake of description.

The luminance signal component of an image separated from the aforementioned TV signal is indicated as a

DATA signal for convenience' sake. This DATA signal is entered into a shift register 104.

The shift register 104 performs serial-parallel conversion for each line of an image with reception of DATA signals serially supplied in time sequence and operates based on the control signal Tsft sent from the control circuit 103. Namely, the control signal Tsft can also be called as a shift clock for the shift register 104.

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Data of one line of an image after the serialparallel conversion (corresponding to driving data for
N devices out of the electron-emitting devices) is
outputted as N parallel signals of Id1 to Idn from the
shift register 104.

A line memory 105 is a storage device for storing the data of one line of an image for a required time and is configured to store the contents of Id1 to Idn properly according to the control signal Tmry sent from the control circuit 103. The stored contents are outputted as I'd1 to I'dn to enter a modulation signal generator 107.

The modulation signal generator 107 is a signal source for appropriately modulating each of the electron-emitting devices of the present embodiment according to each of the image data I'dl to I'dn, and output signals therefrom are applied through terminals Doyl to Doyn to the electron-emitting devices of the

present embodiment in the display panel 101.

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As described previously, the electron-emitting devices according to the embodiment of the present invention have the following basic characteristics concerning the emission current Ie.

Namely, there is the definite threshold voltage Vth for the emission of electrons and electrons are emitted only when a voltage not less than Vth is applied.

threshold, the emission current also varies according to variation in the applied voltage to the devices.

For this reason, when the pulse voltage is applied to the instant devices, for example, electrons are not emitted with application of a voltage not more than the electron emission threshold but an electron beam is outputted with application of a voltage not less than the electron emission threshold.

On that occasion, the intensity of the output electron beam can be controlled by varying the peak height Vm of pulses. It is also possible to control the total charge amount of the output electron beam by changing the width Pw of pulses.

Accordingly, either of the voltage modulation method, the pulse width modulation method, etc. can be employed as a method of modulating the electron-emitting devices according to input signals. For

carrying out the voltage modulation method, the modulation signal generator 107 can be a circuit of the voltage modulation method configured to generate voltage pulses of a fixed length and modulate peak heights of pulses adequately according to input data.

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For carrying out the pulse width modulation method, the modulation signal generator 107 can be a circuit of the pulse width modulation method configured to generate voltage pulses of a fixed peak height and modulate widths of the voltage pulses adequately according to input data.

The shift register 104 and the line memory 105 are of the digital signal type.

The modulation sinal generator 107 is, for example, a D/A converting circuit and an amplifying circuit or the like is added thereto as occasion demands. In the case of the pulse width modulation method, the modulation signal generator 107 is, for example, a circuit consisting of a combination of a fast oscillator and a counting device (counter) for counting the number of waves from the oscillator with a comparing device (comparator) for comparing an output value of the counter with an output value of the memory.

25 The configuration of the image-forming apparatus stated herein is just an example of the image-forming apparatus to which the present invention is applicable,

and a variety of modifications can be made based on the technical concept of the present invention. The input signals were of the NTSC system, but the input signals are not limited to this system; for example, it is also possible to employ the PAL system, SECAM system, etc., and systems of TV signals consisting of a larger number of scanning lines than them (for example, high-definition TV systems including the MUSE system). Examples

More specific examples based on the above embodiments will be described below in detail.

(Example 1)

In the present example, the basic configuration is comprised of the configuration shown in Figs. 1A and 1B as described in the above-stated embodiment.

The steps for fabrication of the electron-emitting device according to the present example will be described below in detail with reference to Figs. 5A to 5E.

20 (Step 1)

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After a silica substrate used as the substrate 1 was cleaned well, a Ti layer 5 nm thick and a Pt layer 500 nm thick, not shown, were first consecutively evaporated over the entire surface of the substrate by sputtering, in order to form the extraction electrode 2 and the negative electrode 3.

Then a resist pattern was formed with an

unrepresented positive photoresist (AZ1500 available from Clariant) by the photolithography process.

Using the patterned photoresist as a mask, the Pt layer and Ti layer were then subjected to dry etching with Ar gas to pattern the extraction electrode 2 and the negative electrode 3 with the electrode gap (the width of gap) of 5 µm (a state shown in Fig. 5A).

The patterning of a thin film or a resist by the photolithography process, film formation, lift-off, etching, etc. will be referred to hereinafter simply as patterning.

(Step 2)

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Then an unrepresented Cr layer was deposited in the thickness of about 100 nm over the entire surface of the substrate by electron beam evaporation and the positive photoresist (AZ1500 available from Clariant) was patterned thereon.

Using the patterned photoresist as a mask, a region (100 μ m \times 80 μ m) to cover the conductive layer for growth of fibrous carbons through the catalyst particles was then formed on the negative electrode 3 and the Cr layer in the opening portion was removed with a cerium nitrate based etchant.

Then a Ti layer for growth of fibrous carbons through the catalyst particles was evaporated in the thickness of 50 nm by sputtering.

Then the unnecessary Ti layer and resist were

removed simultaneously (lift-off method), thereby forming the Ti conductive layer 5 (a state shown in Fig. 5B).

(Step 3)

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By the patterning similar to step 2, the Ti conductive layer 5 was covered by the Ta conductive layer 6 (140 μ m × 100 μ m) not permitting the growth of fibrous carbons through the catalyst particles, so as to expose only the side wall of the Ti conductive layer 5 on the extraction electrode side (a state shown in Fig. 5C).

(Step 4)

In the subsequent step, an unrepresented Cr layer of about 100 nm was patterned so as to expose only side walls of the Pt/Ti layers (equivalent of the negative electrode 3), the Ti conductive layer 5, and the Ta conductive layer 6 on the extraction electrode side.

Then a complex solution obtained by adding isopropyl alcohol or the like to a Pd complex was applied onto the entire surface of the substrate by spin coating.

After the application, a heat treatment was carried out at 300°C in the atmosphere to form a palladium oxide layer in the thickness of about 10 nm over the entire surface. Thereafter, Cr was removed with the cerium nitrate based etchant to lift off the unnecessary palladium oxide thereby, thus forming the

patterned palladium oxide layer.

After evacuation of atmosphere, the substrate was heated to 200°C to carry out a heat treatment in a 2% hydrogen stream diluted with nitrogen. At this stage the catalyst particles 52 were formed in particle diameters of about 3 to 10 nm on the wall surfaces in the surface of device. The density of the particles at this time was estimated as about 10¹¹ to 10¹² particles/cm² (a state shown in Fig. 5D).

10 (Step 5)

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In the subsequent step, a heat treatment was conducted at 500°C in a 0.1% ethylene stream diluted with nitrogen for ten minutes. The resultant was observed with the scanning electron microscope and it was verified therefrom that a number of fibrous carbons 4 extending in fibrous shape as bent were formed in the diameters of about 10 nm to 25 nm only on the wall surface of the Ti conductive layer 5 permitting the growth of fibrous carbons through the catalyst particles among the catalyst particles on the wall surfaces.

The thickness of the fibrous carbons 4 at this time was about 500 nm. No fibrous carbon 4 was recognized on the wall surfaces of the Pt layer (negative electrode 3) and the Ta conductive layer 6 not permitting the growth of fibrous carbons through the catalyst particles (a state shown in Fig. 5E).

The electron-emitting device fabricated as described above was set in the vacuum chamber 60 as shown in Fig. 6 and the interior thereof was evacuated well down to the vacuum of 2 \times 10⁻⁵ Pa by the evacuator 65.

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Then the anode voltage of Va = 10 kV was applied to the positive electrode (anode) 61 H = 2 mm apart from the device, as shown in Fig. 6. At this time, while the pulse voltage consisting of the driving voltage (the voltage placed between the electrodes 2, 3) Vf = 20 V was applied to the device, the flowing device current If and electron emission current Ie were measured.

The If and Ie characteristics of the device were those shown in Fig. 7. Namely, Ie demonstrated a sudden increase from about half of the applied voltage and the electron emission current Ie of about 1 µA was measured at Vf of 15 V. On the other hand, If was similar to the characteristic of Ie but values thereof were a figure or more smaller than those of Ie.

The resultant beam was approximately of a rectangular shape slender in the Y-direction and short in the X-direction.

Beam widths were measured under such conditions
that the voltage (Vf) placed between the negative
electrode 3 and the gate electrode 2 was fixed at 15 V,
the anode distance was fixed at H of 2 mm, the anode

voltage was either of 5 kV and 10 kV, and the gap (width of gap) was either of 1 μ m and 5 μ m, and the results are presented in Table 1 below.

TABLE 1

	Va = 5 kV	Va = 10 kV
Gap : 1 μm		X-direction 30 µm Y-direction 150 µm
Gap : 5 μm	X-direction 93 μm Y-direction 170 μm	X-direction 72 μm Y-direction 150 μm

It was feasible to change the electric field necessary for the driving, by varying the growth conditions. Particularly, an average particle size of Pd particles obtained by the reduction treatment of palladium oxide is associated with the diameters of fibers formed by the growth thereafter.

The mean particle size of Pd particles was able to be controlled by the Pd concentration of the coated Pd complex and the rotational speed of the spin coating.

The carbon fibers of this device were observed with the transmission electron microscope and they were of the layered structure of graphens as shown on the right side of Fig. 12. The layer intervals of the graphens (in the direction of C-axis) were unclear at the temperature as low as about 500°C, and were 0.4 nm. As the temperature increased, the grating intervals became clearer, and at 700°C the intervals were 0.34 nm, which was close to 0.335 nm of graphite.

By employing the configuration of the electron-

emitting device according to the present example, as described above, the electron-emitting device was realized with the properties of the reduced capacitance and driving voltage, the high efficiency, and the small beam size.

(Example 2)

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The electron-emitting device according to Example 2 will be described below with reference to Figs. 2A and 2B. Figs. 2A and 2B are schematic views of the electron-emitting device according to Example 2 of the present invention, wherein Fig. 2A is a plan view thereof and Fig. 2B a cross-sectional view along 2B-2B in Fig. 2A.

The electron-emitting device in the present example was fabricated in the same manner as in Example 1 in the structure and others except that the thickness of the extraction electrode 2 in Example 1 was changed to 200 nm, and If and Ie were measured therewith.

In the structure of the instant device, the thickness of the negative electrode 3 was larger than the thickness of the extraction electrode 2 whereby the electron emission position was able to be set surely at a higher position (on the anode side) from the extraction electrode 2.

25 This configuration decreased the number of electrons flying in the trajectories colliding with the gate, so as to be able to prevent the phenomena of

decrease of efficiency and increase of the beam size.

As a consequence, in the structure of the present device, the electron emission current Ie of about 1 µA was also measured at Vf of 20 V. On the other hand, If was similar to the characteristic of Ie but values thereof were two figures smaller than those of Ie. The beam sizes at this time were also approximately the same as in Table 1.

By employing the configuration of the electronemitting device according to the present example, as described above, the electron-emitting device was realized with the properties of the reduced capacitance and driving voltage, the high efficiency, and the small beam size.

15 (Example 3)

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The electron-emitting device according to Example 3 will be described with reference to Figs. 3A and 3B. Figs. 3A and 3B are schematic views of the electron-emitting device according to Example 3 of the present invention, wherein Fig. 3A is a plan view thereof and Fig. 3B a cross-sectional view along 3B-3B in Fig. 3A.

In the present example, the conductive layer 5 was formed up to an almost middle point of the gap across the gap from on the surface of the negative electrode 3 to on the surface of the substrate in step 2 in Example 1, whereby the gap distance was made to about half.

Since in the present device the gap distance was

smaller than in Example 1, the electric field was about two times stronger than in Example 1. This permitted the voltage for the driving to be reduced to about 8 V. Since the conductive layer 5 was used as an electrical connection layer for the fibrous carbons 4, it became feasible to emit electrons stably from the fibrous carbons 4 in the gap.

By employing the configuration of the electronemitting device according to the present example, as described above, the electron-emitting device was realized with the properties of the reduced capacitance and driving voltage, the high efficiency, and the small beam size.

(Example 4)

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The electron-emitting device according to Example 4 will be described with reference to Figs. 4A and 4B. Figs. 4A and 4B are schematic views of the electron-emitting device according to Example 4 of the present invention, wherein Fig. 4A is a plan view thereof and Fig. 4B a cross-sectional view along 4B-4B in Fig. 4A.

The present example is different as follows in step 1 and step 2 described in foregoing Example 1, and the other steps of the present example are the same as in Example 1.

25 (Step 1)

After the silica substrate used as the substrate 1 was cleaned well, consecutive evaporation by sputtering

was conducted to form a Ti layer 5 nm thick and a Pt layer 500 nm thick as the cathode (emitter) electrode 3 and a Ti layer 100 nm thick as the conductive layer 5 permitting the growth of fibrous carbons.

Then a resist pattern was formed with the positive photoresist (AZ1500 available from Clariant) by the photolithography process.

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Using the patterned photoresist as a mask, the Ti conductive layer 5 was then etched by dry etching with CF₄ and thereafter the Pt and Ti layers were etched by dry etching with Ar, thereby forming the negative electrode 3.

Using the negative electrode 3 as a mask, the silica substrate was etched to the depth of about 500 nm with mixed acids consisting of hydrofluoric acid and ammonium fluoride.

Subsequently, a Ti layer 5 nm thick and a Pt layer 30 nm thick were again consecutively evaporated as the extraction electrode 2 by sputtering. The photoresist on the negative electrode 3 was removed and thereafter a resist pattern was again formed for formation of the gate electrode shape with the positive photoresist (AZ1500 available from Clariant).

Using the patterned photoresist as a mask, the Pt

layer and the Ti layer were then etched by dry etching
with Ar to form the extraction electrode 2 in such
structure that a step difference between steps acted as

a gap.

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Then a resist pattern was formed on the cathode and fine particles of Ni were formed in the thickness of about 5 nm by resistance heating evaporation with good straight-ahead nature. After that, an oxidation treatment was carried out at 350°C for 30 minutes. The steps after this step were the same as those in Example 1.

The configuration of this device permitted formation of a finer gap and made it feasible to emit electrons from about 6 V.

Since the height of the electron-emitting material (film thickness) was large, electrons were not emitted only from the upper part of the film but were also emitted from the middle point, so as to be able to prevent the decrease of efficiency and the increase of the beam size due to the collision of electrons with the gate electrode.

(Example 5)

An image-forming apparatus comprised of a plurality of electron-emitting devices according to the above examples will be described.

The electron-emitting devices of Example 1 were arrayed in a matrix pattern as shown in Fig. 8, thus completing the electron source substrate 81.

Using this electron source substrate 81, the positive electrode (anode) substrate 96 having the

fluorescent member 94 was placed at the distance of 2 mm above the electron-emitting devices 84, thus fabricating the image-forming apparatus shown in Fig. 9.

When the apparatus was driven by the pulse voltage of Vf = 20 V and Va (voltage applied to the anode) = 10 kV, the properties similar to those in Example 1 were also yielded in the image-forming apparatus.

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According to the present invention, as described above, the fibrous carbons are grown only on the side wall surface of the conductive layer on the extraction electrode side, whereby it is feasible to decrease electrons emitted from the other surfaces than the conductive layer, to enhance the electron emission efficiency, and to improve convergence of trajectories of emitted electrons.

When the electron-emitting devices superior in the electron emission efficiency and in the convergence of electron trajectories as described are applied to the electron source, the electron source can be realized with high quality. When this electron source is applied to the image-forming apparatus, the image-forming apparatus can implement formation of higher definition images.

WHAT IS CLAIMED IS:

- 1. An electron-emitting device comprising:
- (A) an extraction electrode and a negative electrode formed in opposition to each other with a gap between said extraction electrode and said negative electrode on an electrically insulating substrate;
- (B) a first layer formed on said negative electrode and having an oxide of Ti, an oxide of Zr, or an oxide of Nb on a surface thereof; and
- (C) a fibrous carbon grown through a catalyst particle disposed on a side wall surface of said first layer on the extraction electrode side.
- 2. The electron-emitting device according to 15 Claim 1, wherein only the side wall surface of said first layer on the extraction electrode side is exposed and the other surfaces thereof are covered with a material on which a fibrous carbon does not grow as compared with said first layer.

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3. The electron-emitting device according to Claim 2, wherein said material on which a fibrous carbon does not grow as compared with said first layer, is at least either one of Ta, Cr, Au, Ag, Pt, and materials of the same kind as a material making said catalyst particle.

4. The electron-emitting device according to Claim 1, wherein said fibrous carbon consists of a graphite nanofiber, a carbon nanotube, an amorphous carbon, or a mixture thereof.

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- 5. The electron-emitting device according to Claim 1, wherein said fibrous carbon comprises a graphen.
- 6. The electron-emitting device according to Claim 1, wherein said fibrous carbon comprises a plurality of graphens.
- The electron-emitting device according to
 Claim 6, wherein said plurality of graphens are layered in an axis direction of said fibrous carbon.
- 8. The electron-emitting device according toClaim 1, wherein said catalyst particle consists of Pd,Ni, Fe, Co, or an alloy thereof.
 - 9. The electron-emitting device according to Claim 1, wherein an electron emission position from said fibrous carbon is more distant from a surface of said substrate than a position of a surface of said extraction electrode.

10. The electron-emitting device according to Claim 1, wherein said extraction electrode and negative electrode are formed on a surface of substantially planar shape of said substrate and a thickness of said negative electrode is larger than a thickness of the extraction electrode.

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- 11. The electron-emitting device according to

 Claim 1, wherein said substrate is thicker in a region

 where said negative electrode is formed than in a

 region where said extraction electrode is formed.
 - 12. The electron-emitting device according to
 Claim 1, wherein said conductive layer is formed from
 on said negative electrode to inside of the gap between
 said extraction electrode and negative electrode on a
 surface of said substrate.
- 13. An electron source wherein a plurality of
 20 electron-emitting devices as set forth in either one of
 Claims 1 to 12 are arrayed.
 - 14. The electron source according to Claim 13, wherein said plurality of electron-emitting devices are electrically connected to a matrix wiring pattern.
 - 15. An image-forming apparatus wherein an image-

forming member for forming an image by collision of emitted electrons is disposed at a position where the image-forming member faces the electron source as set forth in Claim 13.

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- 16. An electron-emitting device comprising:
- (A) a first electrode and a second electrode placed in opposition to each other with a gap between said first and second electrodes on a surface of a substrate; and
- (B) a plurality of fibers electrically connected to said first electrode and comprising carbon as a main component,

wherein said fibers are placed on a surface of said first electrode facing said second electrode.

17. The electron-emitting device according to Claim 16, wherein each of the fibers comprising the carbon as a main component comprises a graphen.

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18. The electron-emitting device according to Claim 16, wherein each of the fibers comprising the carbon as a main component comprises a plurality of graphens.

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19. The electron-emitting device according to Claim 18, wherein said plurality of graphens are

layered in an axis direction of the fiber comprising carbon as a main component.

20. The electron-emitting device according to Claim 16, wherein electrons are emitted by applying a voltage between said second electrode and said first electrode so that a potential of said second electrode is higher than that of the first electrode.

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- 21. The electron-emitting device according to
 Claim 16, wherein a height from said substrate surface
 to said fibers is larger than a height from said
 substrate surface to a surface of the second electrode.
- 15 22. The electron-emitting device according to Claim 16, wherein a thickness of said first electrode is larger than a thickness of said second electrode.
- 23. The electron-emitting device according to
 20 Claim 16, wherein a first layer is placed between said
 first electrode and said fibers and said first layer
 comprises a Ti oxide, a Zr oxide, or an Nb oxide on a
 surface thereof.
- 25 24. The electron-emitting device according to Claim 23, wherein said fibers comprising carbon as a main component are fibers grown through a catalyst

material placed on said first layer.

- 25. The electron-emitting device according to Claim 24, wherein said catalyst material is either of Pd, Ni, Fe, Co, or an alloy thereof.
- 26. The electron-emitting device according to Claim 23, wherein said first layer is electrically conductive.

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- 27. The electron-emitting device according to Claim 23, wherein said first layer is covered by a second layer over the surfaces other than a surface facing said second electrode and said second layer consists of a material on which no substantial growth of fibers comprising carbon as a main component occurs as compared with said first layer.
- 28. The electron-emitting device according to

 Claim 23, wherein said first layer is covered by a

 second layer over the surfaces other than a surface
 facing said second electrode and said second layer

 consists of a material selected from Ta, Cr, Au, Ag,

 Pt, and materials of the same kind as a catalyst

 material.
 - 29. An electron source wherein a plurality of

electron-emitting devices as set forth in either one of Claims 16 to 28 are arrayed.

30. An image-forming apparatus comprising the electron source as set forth in Claim 29, and a fluorescent member.

ABSTRACT OF THE DISCLOSURE

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Provided are electron-emitting devices, electron sources, and image-forming apparatus improved in electron emission efficiency and in convergence of trajectories of emitted electrons. An electronemitting device has a first electrode and a second electrode placed in opposition to each other with a gap between first and second electrodes on a surface of a substrate, and a plurality of fibers electrically connected to the first electrode and containing carbon as a main component, and the fibers are placed on a surface of the first electrode facing the second electrode.

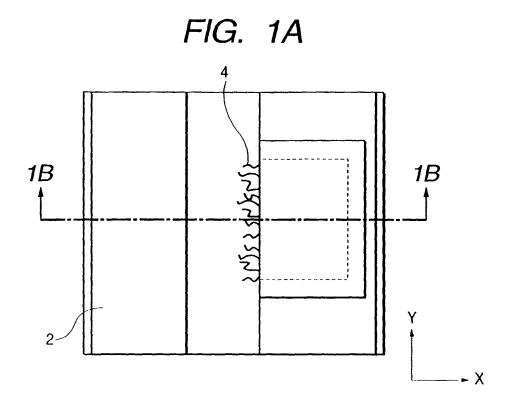
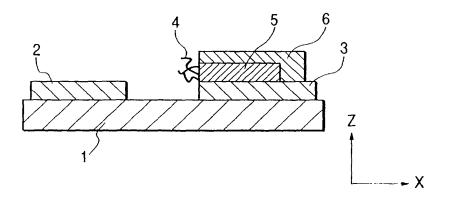


FIG. 1B



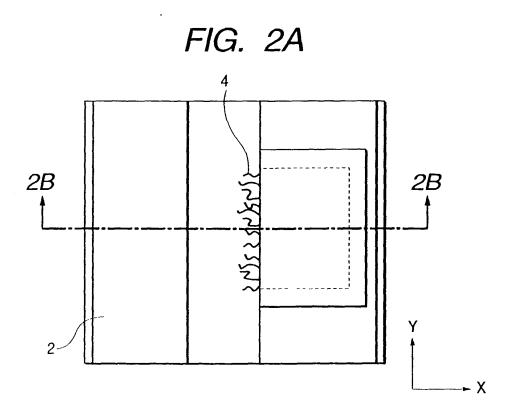


FIG. 2B

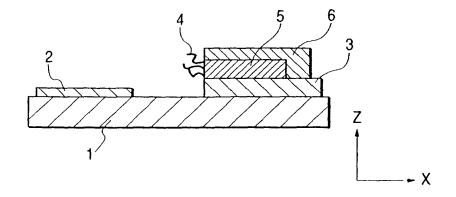


FIG. 3A

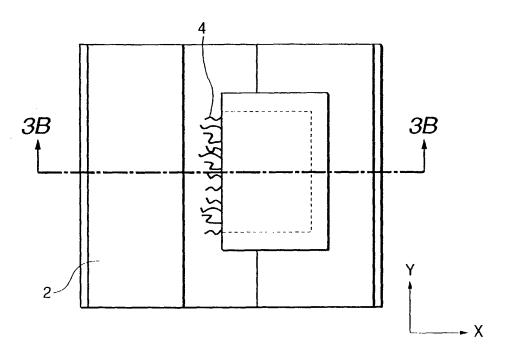
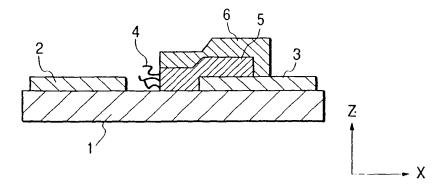
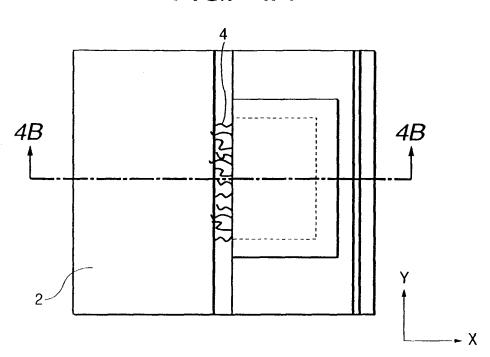
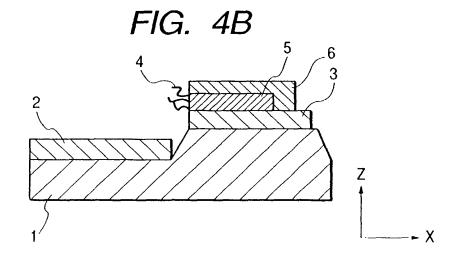


FIG. 3B









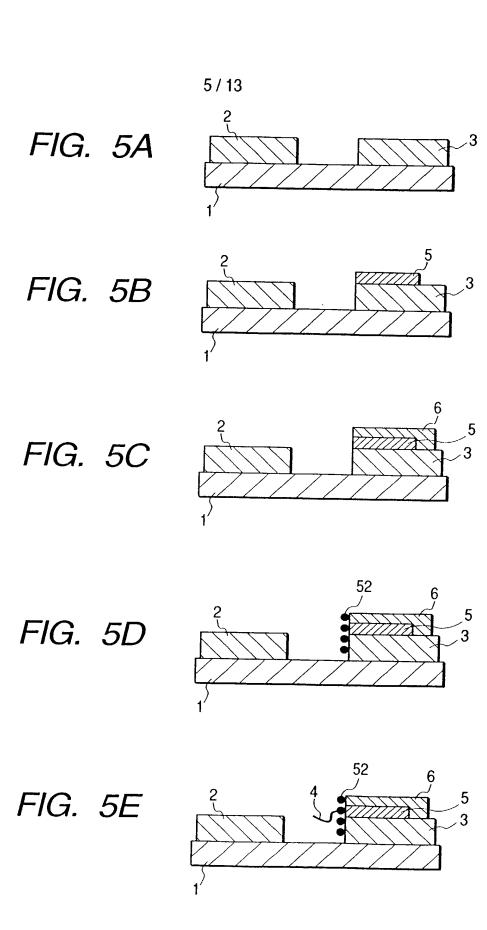


FIG. 6

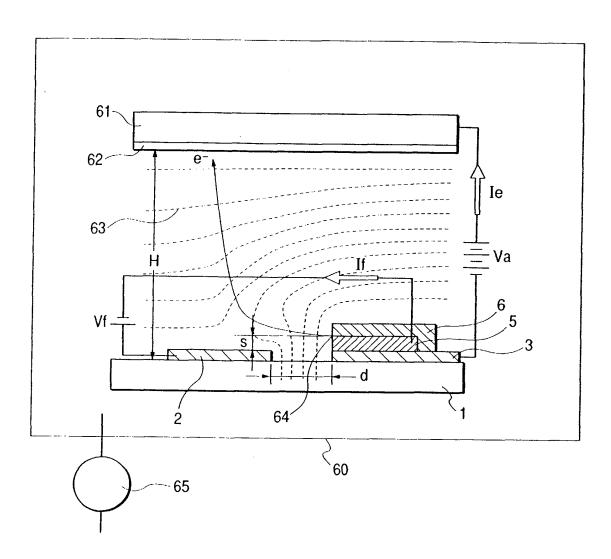


FIG. 7

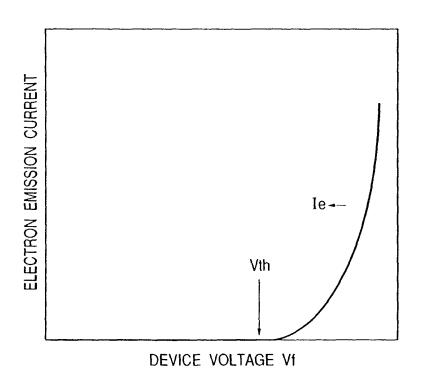
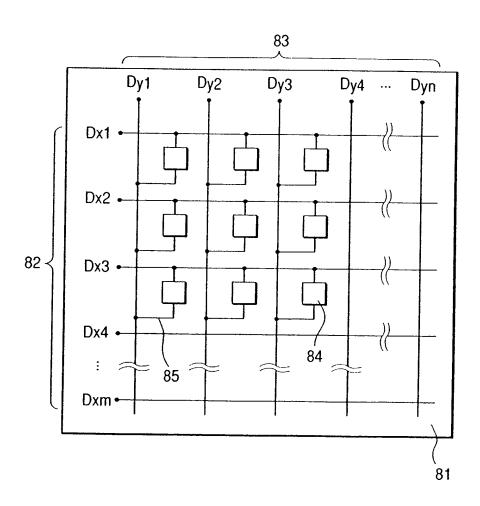


FIG. 8



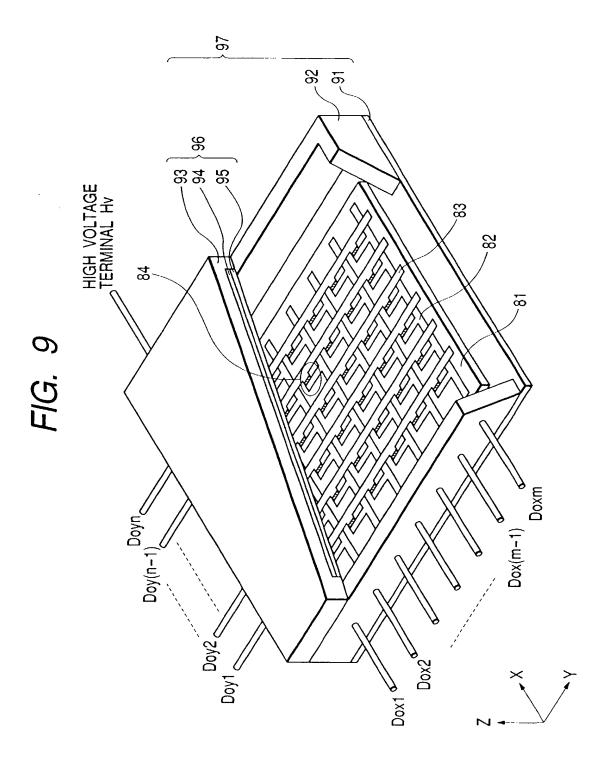


FIG. 10

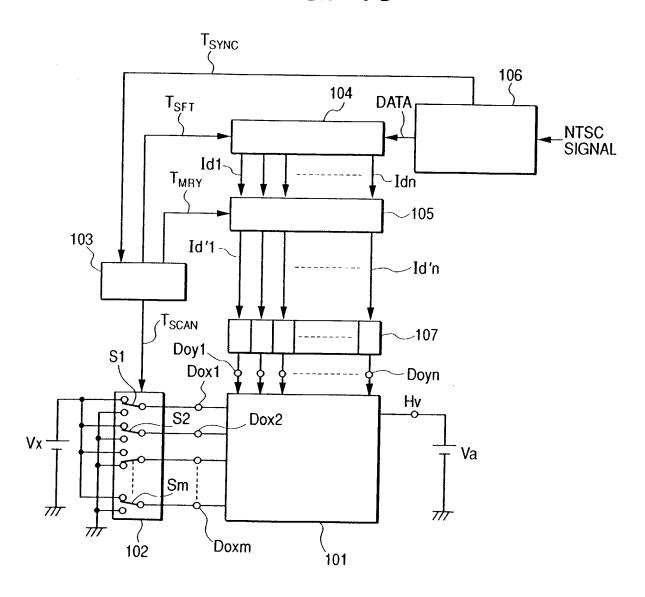


FIG. 11

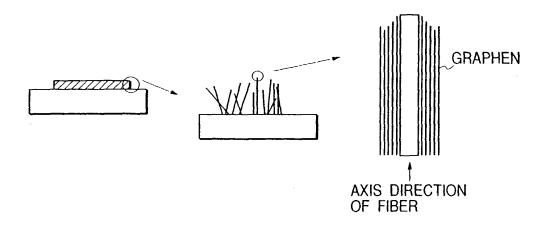


FIG. 12

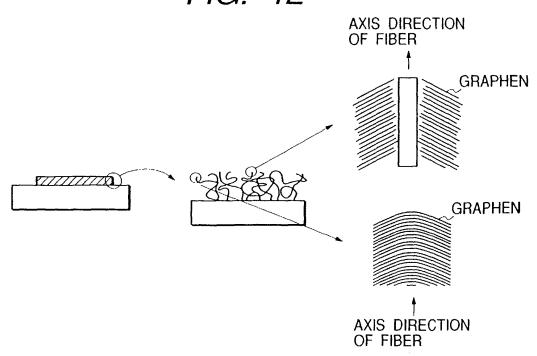


FIG. 13

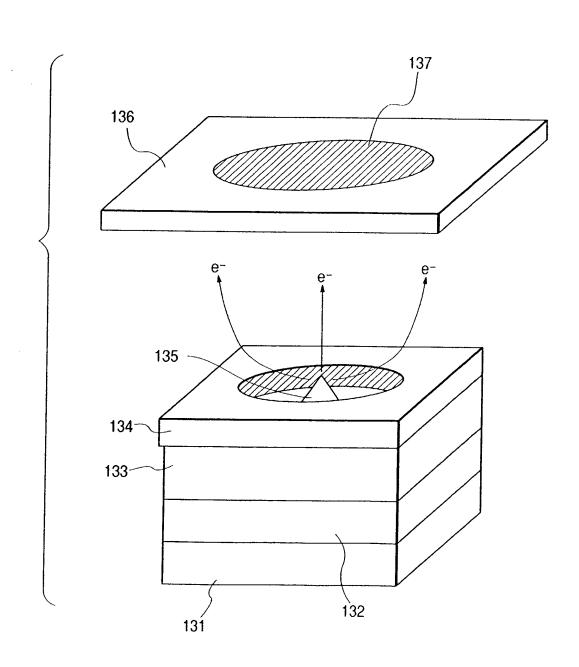
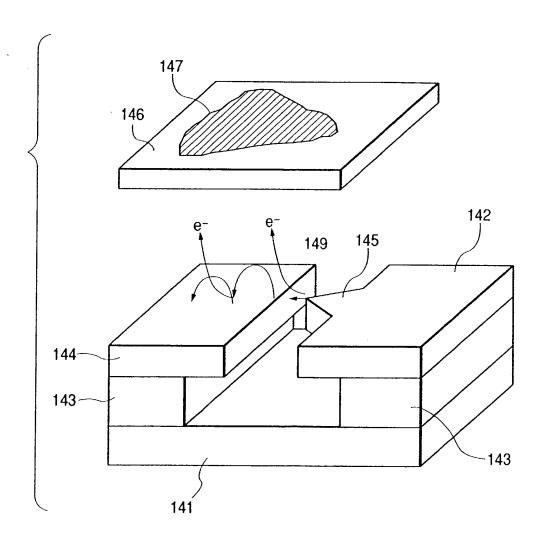


FIG. 14



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ELECTRON-EMITTING DEVICE, ELECTRON SOURCE, IMAGE-O-AU J & 52

FORMING APPARATUS, AND METHOD FOR PRODUCING ELECTRONEMITTING DEVICE AND ELECTRON-EMITTING APPARATUS

5 BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to an electronemitting device, an electron source using therewith, an image-forming apparatus, and a method for producing an electron-emitting device.

Related Background Art

A field emission type (FE-type) electron-emitting device for emitting an electron from a metal surface with a strong field over 10⁶ V/cm applied to the metal has attracted attention as one of the effective cold electron sources.

If an FE-type cold electron source is put to practical use, a thin-type emissive image display device can be realized, thereby contributing to a power saving and lightweight system.

FIG. 12 shows a vertical FE-type structure. In FIG. 12, reference numeral 121 denotes a substrate, reference numeral 123 denotes an emitter electrode, reference numeral 124 denotes an insulation layer, reference numeral 125 denotes an emitter, reference numeral 126 denotes an anode, and reference numeral 127 denotes the shape of an electron beam emitted to the

anode. An aperture is formed in the layers of the insulation layer 124 and a gate electrode 122 arranged on the cathode electrode 123. The conical emitter 125 is provided in the aperture (the structure is hereinafter referred to as a Spindt type structure). The structure is disclosed by, for example, C. A. Spindt, "Physical Properties of thin-film field emission cathodes with molybdenum cones", J. Appl. Phys., 47,5248 (1976), etc.

10 Furthermore, an example of a lateral FE-type electron-emitting device can be formed by an emitter electrode having a pointed end and a gate electrode (extracting electrode) for extracting an electron from the end of the emitter electrode arranged parallel to the substrate with a collector (referred to as an anode in the present invention) provided in the direction vertical to the opposing direction of the gate electrode and the emitter electrode.

An example of an electron-emitting device using a 20 fibrous carbon is disclosed by Japanese Patent Application Laid-Open No. 8-115652, Japanese Patent Application Laid-Open No. 2000-223005, European Patent Publication EP-A1-1022763, etc.

25 SUMMARY OF THE INVENTION

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In the image-forming apparatus using the above mentioned FE-type electron source, an electron beam

spot (hereinafter referred to as a beam diameter) can be obtained depending on the distance H from the electron source to the phosphor, the anode voltage Va between the electron-emitting device and the phosphor, the device voltage Vf between the cathode electrode and the leading electrode. The above mentioned beam span is submillimeter, and has sufficient resolution as an image-forming apparatus.

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However, in the image-forming apparatus such as an image display device, etc., resolution with higher precision has been requested recently.

Furthermore, with an increasing number of displayed pixels, power consumption has risen from a large device capacity of the electron-emitting device when it is driven. Therefore, it has been demanded to reduce the device capacity and the device voltage, and improve the efficiency of the electron-emitting device.

Furthermore, it is necessary to have uniform characteristic of the electron-emitting device to avoid uneven distribution of the brightness among the pixels due to the uneven characteristics of the electron-emitting devices.

As a result, it is requested to reduce the capacity of a device, the device voltage, and the uneven characteristics among electron-emitting devices.

In the Spindt-type electron-emitting device shown in FIG. 12, a parasitic capacity has been formed

between a large gate capacity and a number of emitters 125 by the layer structure of a gate electrode 122 and a substrate 121. Furthermore, the device voltage of the spindt-type FE is as high as several tens of V, thereby causing the problem of large power consumption from a large capacity.

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Additionally, since extracted electron beams diffuse, a focusing electrode has been required to suppress the diffusion of the beams. For example, Japanese Patent Application Laid-Open No. 07-006714 discloses a method of focusing the trajectory by providing an electrode for focusing electrons. However, this method has the problem that the process step of assigning the focusing electrode is complicated, and that the electron emission efficiency is low.

Furthermore, since a common horizontal FE is designed such that an electron emitted from a normal cathode easily crashes against the gate electrode, the efficiency (the ratio of the electric current flowing through a gate to the electric current reaching the anode) is lowered, and the beams largely diffuse at the anode.

With electron-emitting devices formed by a set of fibrous carbon, local electron emission (electric field concentration) is apparent when there are large differences in length and shape among the devices.

Therefore, the current density accompanied by the electron emission becomes high at a portion where local electric field concentration arises, thereby possibly deteriorating the electron emission characteristic and shortening the life of the device.

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Additionally, with the image-forming apparatus having a plurality of the above mentioned devices, the above mentioned events cause the apparent distribution of the amount of Ie (emission current) of each electron-emitting device, thereby reducing the performance of the image-forming apparatus by resulting in the poor display of gray scale images, flickering images, etc.

The present invention has been developed to solve the above mentioned problems, and aims at providing a durable electron-emitting device, electron source, image-forming apparatus having a uniform display characteristic for a long period, and a method for easily producing the electron-emitting device and the image-forming apparatus by guaranteeing a uniform electron emission characteristic.

To attain the above mentioned purpose, the method for producing an electron-emitting device according to the present invention includes on the surface of a substrate the steps of: arranging a cathode electrode; arranging an electrode opposite the cathode electrode; arranging a plurality of fibers mainly made of carbon

on the cathode electrode; and applying higher potential to the electrode opposite the cathode electrode than the potential applied to the cathode electrode under the depressurized condition.

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Another method for producing the electron source according to the present invention to attain the above mentioned purpose includes the steps of: arranging on the substrate a plurality of electron-emitting devices each having a plurality of fibers mainly made of carbon, and a plural pieces of wire each being electrically connected to at least one of the plurality of electron-emitting devices; applying a voltage to at least a part of the plurality of electron-emitting devices and measuring the electric characteristic of the electron-emitting device to which the voltage has been applied; and reducing the difference in electric characteristic among the plurality of electron-emitting devices based on the measurement result. The step of reducing the difference in characteristic among the above mentioned plurality of electron-emitting devices includes the step of allowing electrons to be emitted from at least one of the plurality of electron-emitting devices under the depressurized condition.

Furthermore, it is preferable that the step of emitting an electron from the above mentioned electron-emitting device is performed under the condition of a gas physically or chemically reactive to the fiber. In

this process, the portion where an electric field concentrates in the fiber is made to be reactive for a partial etching process. As a result, the stable and uniform electron-emitting device, electron source, and image-forming apparatus can be produced.

It is preferable that the gas chemically reactive to the fiber contains H_2 , H_2O , O_2 , or CO_2 . Otherwise, it is desired that the gas chemically reactive to the fiber is a combination of H_2 gas and one of H_2O , O_2 , and CO_2 gas.

BRIEF DESCRIPTION OF THE DRAWINGS

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FIGS. 1A, 1B, 1C, 1D and 1E show a method for producing an electron-emitting device according to the first embodiment;

FIGS. 2A and 2B show a step of equalizing the shapes of fine projections among the electron-emitting devices according to an embodiment of the present invention;

20 FIGS. 3A and 3B show an electron-emitting device according to the embodiment of the present invention;

FIGS. 4A, 4B, 4C and 4D show the step of producing the electron-emitting device according to the embodiment of the present invention;

FIGS. 5A and 5B show a change with time of an emission current of an electron-emitting device;

FIG. 6 shows an example of the configuration when

an electron-emitting device is operated;

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- FIG. 7 shows an example of the operation characteristic of an electron-emitting device according to the embodiment of the present invention;
- FIG. 8 shows an example of the configuration of a simple matrix circuit according to the embodiment of the present invention;
 - FIG. 9 shows an example of the configuration of an image-forming apparatus using the electron source according to the embodiment of the present invention;
 - FIG. 10 shows the outline of the structure of a carbon nanotube;
 - FIG. 11 shows the outline of the structure of a graphite nanofiber;
- 15 FIG. 12 shows the conventional vertical FE-type electron-emitting device;
 - FIG. 13 shows the type of an equalizing process according to the present invention; and
- FIG. 14 shows the type of another equalizing process according to the present invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The preferred embodiments of the present invention are described below in detail by referring to the attached drawings. However, the present invention is not limited to the dimensions, materials, shapes, and relative arrangements of the components of the

embodiments unless otherwise specified.

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Described first below is the equalizing process of the electron emission characteristic of an electronemitting device.

According to the present invention, it is most desirable to use fibrous carbon as an electron-emitting member of an electron-emitting device. Since fibrous carbon has a very large aspect ratio, it easily enhances an electric field. Therefore, it is possible to emit an electron at a low voltage, and the fibrous carbon is recommended as an electron-emitting member according to the present invention.

The "fibrous carbon" according to the present invention can refer to a "columnar substance chiefly made of carbon" or "linear substance chiefly made of carbon". Furthermore, the "fibrous carbon" can also be referred to as "fiber chiefly made of carbon". To be more practical, the "fibrous carbon" according to the present invention also includes carbon nanotube, graphite nanofiber, and amorphous carbon fiber.

Especially, graphite nanofiber is the most desirable as an electron-emitting member.

However, when the fibrous carbon is used as an electron-emitting member, it is frequently used as a set of plural pieces of fibrous carbon in consideration of the production method. Since it is very difficult to equalize the shapes of the fibrous carbon in

thickness, length, etc., there often occurs unevenness in characteristic among the electron-emitting devices if the set of plural pieces of fibrous carbon is used as an electron-emitting member of an electron-emitting device.

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Under the situation, according to the present invention, a process of reducing the difference in electron emission characteristic among electron-emitting devices (equalizing process) is performed to control the electron emission characteristic of the electron-emitting device in which plural pieces of fibrous carbon is used as an electron-emitting member.

The "equalizing process" which is the characteristic of the method for producing the electron-emitting device according to the present invention is performed by applying a voltage to an electron-emitting device after arranging plural pieces of fibrous carbon on the electrode (cathode electrode) to which potential, which is lower than the potential to the opposite electrode (extracting electrode) in a pair of electrodes forming the electron-emitting device when the device is driven, is applied.

This method is especially convenient and effective when an electron source, an image-forming apparatus, etc. are formed using a plurality of electron-emitting devices.

The "equalizing process" according to the present

invention not only reduces the difference in electron emission characteristic among a plurality of electron-emitting devices, but also improves the electron emission characteristic of one electron-emitting device.

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That is, the electron-emitting device immediately after forming fibrous carbon indicates the difference in shape among plural pieces of fibrous carbon. Such a device can form a portion where an electric field specifically concentrates. When such an electron-emitting device having specific electric field concentration is operated, electrons are emitted with concentration from the specific portion, and a load is excessively generated in the portion. As a result, the electron emission characteristic is suddenly damaged, and no sufficient performance of an electron-emitting device can be obtained.

Therefore, by performing the "equalizing process" according to the present invention, the portion in which an electric field specifically concentrates can be removed, and electrons are substantially equally emitted from a number of pieces of fibrous carbon (the number of electron emission sites is increased). As a result, electron-emitting devices having an excellent electron emission characteristic and stable for a long period can be obtained.

It is desired that the above mentioned "equalizing

process" according to the present invention is performed by applying a voltage to a device under the condition of a substance reactive to the fibrous carbon.

5 The principle of the equalizing process is performed by an etching operation using the heat generated when an electron is emitted from the fibrous carbon, which is an electron-emitting portion, into a vacuum. In addition, when the process is performed 10 under the condition of the substance reactive to fibrous carbon, the reactive substance in the condition and the fibrous carbon are selectively reactive to each other, thereby performing a partial etching process.

Since the fibrous carbon chiefly contains carbon, the following reactions occur.

$$C + H_2O \rightarrow H_2\uparrow + CO\uparrow \dots (1)$$

$$C + O_2 \rightarrow CO_2\uparrow \dots (2)$$

$$2C + O_2 \rightarrow 2CO\uparrow \dots (3)$$

$$C + CO_2 \rightarrow 2CO\uparrow \dots (4)$$

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Therefore, H_2O , CO_2 , O_2 , H_2 , etc. can be useful as substances reactive to the fibrous carbon.

FIGS. 2A and 2B shows the type of the equalizing process according to the present invention using a lateral electron-emitting device in which fibrous carbon is used as an electron-emitting member.

In FIGS. 2A and 2B, reference numeral 1 denotes an insulating substrate, reference numeral 2 denotes a

extracting electrode (also referred to as a "second electrode" or "gate electrode"), reference numeral 3 denotes a cathode electrode (also referred to as a "first electrode" or "negative electrode"), reference numeral 4 denotes an electron-emitting member comprising plural pieces of fibrous carbon electrically connected to the cathode electrode. Reference numeral 20 denotes a vacuum chamber, reference numeral 21 denotes a substrate holder, reference numeral 22 denotes a gas leading valve, reference numeral 23 denotes vacuum pump, reference numeral 24 denotes an anode (also referred to as a "third electrode"), and reference numeral 25 denotes an equipotential surface.

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In this example, a lateral electron-emitting device is described, but the producing method according to the present invention is also applicable to a vertical electron-emitting device in which fibrous carbon is used as an electron-emitting member.

Furthermore, since a lateral electron-emitting device is simpler in production, and smaller in capacity in the driving operation than the vertical electron-emitting device, a high-speed driving process can be performed.

Furthermore, although the vertical electronemitting device shown in FIG. 12 includes a cathode
electrode 123 and an extracting electrode (gate
electrode) 125, the fibrous carbon can emit electrons

in a low electric field. Therefore, the present invention can also be applied to a vertical electronemitting device without a gate electrode 125 and an insulating layer 124 shown in FIG. 12. That is, the present invention can be applied to an electronemitting device configured by the cathode electrode 123 provided on the substrate 121 and fibrous carbon provided thereon.

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In the vertical electron-emitting device, an 10 "equalizing process" can be performed by performing the voltage applying process similar to the process performed in the "equalizing process" described later, for applying the voltage between the cathode electrode (reference numeral 123 shown in FIG. 12) where the fibrous carbon is arranged and the anode (reference numeral 126 shown in FIG. 12). Otherwise, an "equalizing process" can also be performed by performing the process similar to the voltage applying process performed in the "equalizing process" described later, for applying the voltage between the extracting electrode (reference numeral 122 shown in FIG. 12) and the cathode electrode provided between the cathode electrode (reference numeral 123 shown in FIG. 12) where the fibrous carbon is arranged and the anode (reference numeral 126 shown in FIG. 12).

Furthermore, an "equalizing process" can also be performed by arranging an electrode plate above the

cathode electrode where the fibrous carbon is provided, and performing a voltage applying process similar to the voltage applying process performed in the "equalizing process" described later between the electrode plate and the cathode electrode.

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The "equalizing process" introduces an "reactive gas" reactive to the fibrous carbon from the gas leading valve 22 after evacuating the vacuum chamber 20 by the vacuum pump 23. Then, a voltage is applied to the electron-emitting member 4 of fibrous carbon such that the extraction electrode 2 can be positive, and an electron is emitted from the electron-emitting member 4 of fibrous carbon. Then, the electron-emitting member 4 of fibrous carbon proceeds with the above mentioned reaction toward right by means of the heat from the electron emission, etc., thereby etching the fibrous carbon (FIG. 2A).

During the process of the above mentioned reaction, the reactive gas on the left side is incessantly introduced by the gas leading valve 22, the product on the right is evacuated by the vacuum pump 23, and the above mentioned reaction expressions are proceeding right.

Since the reaction can be reciprocal, a reaction product is set to be immediately removed from the reaction system.

Furthermore, it is recommended to reserve the time

to stop electron emission to promote the reaction between the reactive gas and the electron-emitting member. To attain this, it is desired that a pulse voltage is applied between the electron-emitting member 4 and the extraction electrode 2.

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Since the reaction is driven by the heat from the electron emission, the portion of the electron-emitting member 4 easily emitting an electron (in which an electric field can be easily enhanced) reacts with concentration to the heat and then be etched in the set of fibrous carbon. As a result, the electric field can be equally applied by an electron emission area by removing the portion where the electric field has excessively been concentrated.

FIG. 2B shows the type of the result of the "equalizing process". After performing the "equalizing process", the electric field difference applied to each piece of fibrous carbon is reduced. That is, the equipotential surface 25 which is largely distorted as 20 shown in FIG. 2A is reduced in distortion as shown in FIG. 2B.

When an image-forming apparatus is provided, etc., the "equalizing process" can also be performed after bonding an electron source substrate formed by a plurality of electron-emitting devices each having fibrous carbon and the wiring for use in driving the electron-emitting devices with a face plate having an

image-forming member comprising a phosphor, etc., and forming a vacuum envelope (referred to as a sealing process).

In the above mentioned process, the performance of the electron-emitting device, electron source, and image-forming apparatus using plural pieces of fibrous carbon can be improved.

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That is, the electron-emitting device according to the present invention prevents the local electric field concentration in the "equalizing process", thereby equalizing the electron emission characteristic, and suppressing the attenuation of the emission current by the overload from the high current density due to the local field concentration.

Therefore, the induction of discharge can be suppressed, the durability of the electron-emitting device can be elongated, and a stable electron emission current with small fluctuations with time can be maintained.

Then, since the electron emission current of each electron-emitting device can be stably maintained in the electron source and the image-forming apparatus including a plurality of electron-emitting devices, the durability of each pixel can be improved, the gray scale of an image can be successfully expressed, and the flicker of the image can be avoided, thereby expressing equal display characteristic for a long

period.

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Described below is an embodiment of the practical configuration according to the present invention.

FIGS. 3A and 3B show an example of the configuration of the electron-emitting device on which the producing method according to the present invention works. FIG. 3A is a plan view of the electron-emitting device according to the present embodiment. FIG. 3B is a sectional view along 3B-3B shown in FIG. 3A.

In FIGS. 3A and 3B, reference numeral 1 denotes a substrate, reference numeral 2 denotes an extracting electrode, reference numeral 3 denotes a cathode electrode, and reference numeral 4 denotes an electron-emitting member. FIGS. 4A to 4D schematically show a type of the method of producing an electron-emitting device according to the present embodiment. An example of the method of producing an electron-emitting device according to the present embodiment is described below by referring to FIGS. 4A to 4D.

The substrate 1 refers to quartz glass, glass whose impure contents such as Na, etc. are reduced and replaced with K, etc., sodalime glass, a layer structure obtained by applying SiO₂ on the silicon substrate, etc. in the spatter method, etc., and an insulating substrate such as ceramics, etc. of alumina, etc. (FIG. 4A).

The extraction electrode (gate electrode) 2 and

the cathode electrode 3 are disposed on the insulating substrate 1 (FIG. 4B).

The extraction electrode 2 and the cathode electrode 3 are conductive, and can be formed by the common vacuum film-forming technology such as the evaporation method, the spatter method, etc. and the photolithography technology.

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The material of the extraction electrode 2 and the cathode electrode 3 can be, for example, carbon, metal, metal nitride, metal carbide, metal boride, semiconductor, or metal compound semiconductor.

The thickness of the electrodes 2 and 3 can be set in the range from several tens nm to several μm . It is desired to use such a heat resistant material as carbon, metal, metal nitride, metal carbide, etc. If the potential can be reduced due to a thin electrode, or if the electron-emitting device is used in a matrix array, then a low resistance metal wiring material can be used in a portion not involved in the electron emission as necessary.

The distance between the extraction electrode 2 and the cathode electrode 3 can be determined depending on the device voltage driving the electron-emitting device between the extraction electrode 2 and the cathode electrode 3 such that the electron emission field can be one through ten times larger than the vertical field when the electron emission field

(lateral field) of the electron-emitting member 4 is compared with the vertical field required to form an image.

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For example, when the distance between the anode 24 and the cathode electrode 3 is 2 mm, and 10 kV is applied, the vertical field is 5 V/ μ m. In this case, the distance and the device voltage are to be determined such that the electron emission field of the electron-emitting member to be used is larger than 5 V/ μ m, and corresponds to be the selected electron emission field.

The "lateral field" according to the present invention can be referred to as a "electric field practically parallel to the surface of the substrate 1", or a "electric field in the direction of the extraction electrode 2 opposite the cathode electrode 3.

The "vertical field" according to the present invention refers to an "electric field in the direction substantially perpendicular to the surface of the substrate 1", or an "electric field in the direction of the substrate 1 opposite an anode electrode 61".

Then, the electron-emitting member 4 having an uneven surface is disposed on the cathode electrode 3 (FIG. 4C). The material used as the electron-emitting member 4 is a set of fibrous carbon. It is desired that the fibrous carbon is graphite fiber.

The above mentioned fibrous carbon has a threshold field of several V/ μm . FIGS. 10 and 11 show an example of configurations of fibrous carbon suitable for the present invention. Each figure shows an embodiment at an optical microscope level (approximately $1000 \times$) on the left, an embodiment at a scanning electronic microscope (SEM) level (approximately $30,000 \times$) in the center, and an embodiment at a transmission electronic microscope (TEM) level

10 (approximately 1 millionx) on the right.

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As shown in FIG. 10, a cylindrical shape of graphen (multiple wall cylinder is referred to as a multiwall nanotube) is referred to as a carbon nanotube, and its threshold is the smallest when the tip of the tube is opened.

FIG. 11 shows the fibrous carbon may be produced at a relatively low temperature. A fibrous carbon of this form is comprised of a lamination of graphens (which is thus sometimes called "graphite nanofiber" and the ratio of the amorphous structure of which increases depending on the temperature). To be more practical, the graphite nanofiber indicates a fibrous substance in which graphens are layered (laminated) in the longitudinal direction (axial direction of fiber). That is, as shown in FIG. 11, it is a fibrous substance in which plurality of graphens are arranged and layered (laminated) so as not to be parallel to the axis of the

fiber.

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The other carbon nanotube is a fibrous substance in which graphens are arranged (in cylindrical shape) around the longitudinal direction (axial direction of fiber). In other words, it is a fibrous substance in which graphens are arranged substantially in parallel to the axis of the fiber.

One sheet of graphite is referred to as a "graphen" or a "graphen sheet". To be more practical, graphite is obtained by laying plural carbon sheets, a lamination in which carbon planes, each of which is a spread of regular hexagons consisting of covalent bonds of carbon atoms in sp² hybrid, are layered at intervals of distance of 3.354 Å. Each of the carbon planes is called a "graphen" or a "graphen sheet".

Either fibrous carbon has an electron emission threshold of 1 V to 10 V/ μm and is recommendable as the material of the emitter (electron-emitting member) 4.

Especially, an electron-emitting device using a set of graphite nanofiber is not limited to the device structure according to the present invention shown in FIGS. 2 and 3, but can emit electrons in a low electric field, can obtain a large emission current, can be easily produced, and obtains an electron-emitting device having a stable electron emission characteristic. For example, a graphite nanofiber emitter is used, an electron-emitting device can be

obtained by preparing an electrode for controlling the electron emission from the emitter, and a light emitting apparatus such as a lamp, etc. can be formed using a light emission member emitting light by the irradiation of an electron emitted from a graphite nanofiber. Furthermore, by arranging plural arrays of electron-emitting devices using the above mentioned graphite nanofiber and by preparing an anode electrode comprising a light emission member such as a phosphor, etc., an image-forming apparatus such as a display, etc. can be configured. An electron-emitting device, a light emitting device, and an image-forming apparatus using graphite nanofiber can stable emit electrons without keeping the inside each device in a vacuum state as in the conventional electron-emitting device. Furthermore, since electrons can be emitted in a low field, a reliable device can be easily produced. As a result, the producing method according to the present invention is more recommendable in the device using the graphite nanofiber.

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The above mentioned fibrous carbon can be formed by decomposing the hydrogen carbide gas using a catalyst (a material for promoting the pile of carbon). The carbon nanotube and the graphite nanofiber depend on the type of catalyst and the temperature of decomposition.

As the catalyst material, Fe, Co, Pd, Ni, or an

alloy of any of the selected materials can be used as the nucleus forming the center of the fibrous carbon.

In particular, Pd, Ni may be material for generating graphite nanofiber at a low temperature (400°C or more). The temperature at which the carbon nanotube is generated using Fe or Co is over 800°C while the graphite nanofiber material can be generated at a low temperature. Therefore, it is desired from the viewpoint of the influence on other members and the production cost to generate graphite nanofiber material using Pd and Ni.

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Furthermore, relating to Pd, using the characteristic of an oxide which is reduced at a low temperature (room temperature), paradium oxide can be used as a nucleus forming material.

When a hydrogen reduction process is performed on a paradium oxide, a fast condensation nucleus can be formed at a relatively low temperature (200° or lower) without thermal condensation of a thin metal film or generation and evaporation of super-particle conventional used as common nucleus forming technology.

The above mentioned hydrogen carbide gas can be, for example, ethylene, methane, propane, propylene, CO, ${\rm CO_2}$ gas, or vapor of an organic solvent such as ethanol, acetone, etc.

Furthermore, the present invention can be applicable to any electron-emitting member 4 having an

uneven surface as shown in FIG. 4C. The material of the electron-emitting member 4 having an uneven surface can be a heat-resistant material such as W, Ta, Mo, etc., a carbide such as TiC, ZrC, HfC, TaC, SiC, WC, etc., a boride such as HfB_2 , ZrB_2 , LaB_6 , CeB_6 , YB_4 , GdB_4 , etc., a nitride such as TiN, ZrN, HfN, etc., a semiconductor such as Si, Ge, etc., carbon and carbon compound, etc. containing diffused amorphous carbon, graphite, diamond-like carbon, and diamond.

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Such a electron-emitting member 4 having an uneven surface can be obtained by either the process of generating projections using a method of the RIE, etc. from a film piled in the common vacuum film-forming method, etc. such as the spatter method, etc. or the process of growing a pin-shaped crystal through the generation of a nucleus in the CVD, growing a whisker-shaped crystal, etc.

The control of the shape of the projections depends on the type of substrate to be used, the type of gas, the pressures of a gas (flow rate), an etching time, the energy when plasma is formed, etc. On the other hand, in the CVD forming method, control is performed based on the type of substrate, the type of gas, the flow rate, the growing temperature, etc.

Regardless of the relation to the electron emission, the area in which the electron-emitting member 4 is placed is referred to as an "electron

emission area" according to the present invention.

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Then, the above mentioned electron-emitting member 4 is partially etched, and the "equalizing process" increasing the number of emission sites is performed (FIG. 4D).

After the electron-emitting device is provided in the vacuum chamber 20 as shown in FIGS. 2A and 2B, and the vacuum chamber 20 is evacuated by the vacuum pump 23, the gas leading valve 22 introduces a substance chemically or physically reactive to the electron-emitting member 4.

A chemically reactive substance can be the above mentioned O_2 , CO, H_2O , H_2 , etc. when the electron-emitting member 4 is carbon (fibrous carbon). It is preferable that the gas chemically reactive to the fiber is a mixed gas of a gas selected from among H_2O , O_2 , CO_2 and H_2 gasses.

A substance physically reactive refers to a substance which can be an electrified particle when an electron beam crashes, and it is desired to have a substance having a large mass such as Ar, etc. The introduction pressure of a gas of the above mentioned substance depends of the type of gas. However, when the substance is chemically reactive, it is 1×10^{-4} Pa or over. When the substance is physically reactive, it is approximately 1×10^{-6} to 1×10^{-4} Pa.

If potential is applied to the electron-emitting

member 4 of the electron-emitting device such that the extraction electrode 2 of the electron-emitting device can be positive, and an electron is emitted after introducing the above mentioned gas, then the above mentioned gas is reactive to the electron-emitting member 4 to etch the electron-emitting member 4.

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In this step in the electron emission area, a portion in which electrons can be easily emitted (an electric field can be easily enhanced) becomes reactive and etched with concentration, a portion in which an electric field has excessively concentrated can be removed, and the field can be more equally applied to the electron emission area.

FIGS. 2A and 2B show the type of this process.

FIG. 2A shows the type of the device when the

"equalizing process" is started, and FIG. 2B shows the

type of the device after performing the "equalizing

process".

When an image-forming apparatus is formed, this step can also be performed by: bonding the electron source substrate on which wiring, etc. is arranged for an electron-emitting device to the face plate having an image-forming member comprising a phosphor, etc.; introducing the reactive gas after forming an envelope (referred to a sealing step); and applying positive potential to the anode in the electron emission area.

Thus, an electron-emitting device according to the

present embodiment can be formed.

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The electron-emitting device and its operation obtained in the above mentioned steps are described below by referring to FIGS. 6 and 7. An electron-emitting device having a gap of several µm between the extraction electrode 2 and cathode electrode 3 is provided in a vacuum chamber 60 as shown in FIG. 6 to allow a vacuum pump 63 to completely perform an evacuation until achieving a pressure of about 10⁻⁵ Pa, the anode electrode 61 is provided at the height of H, which if several mm from the substrate 1, using a high voltage as shown in FIG. 6, and an anode voltage Va, that is, a high voltage of several kV, is applied between the cathode electrode 3 and the anode electrode 61.

A phosphor 62 coated with a conductive film is provided on the anode electrode 61.

 λ device voltage Vf of a pulse voltage of several tens V is applied between the extraction electrode 2 and the cathode electrode 3 to measure a flowing device current If and an electron emission current Ie.

At this time, an equipotential line 66 is formed as shown in FIG. 6, and the point at which an electric field concentrates is located closest to the anode 61 of the electron-emitting member 4 indicated by 64, and inside the gap.

It is assumed that an electron is emitted from the

electron-emitting member 4 located near the electric field concentration point 64.

As shown in FIG. 7, the characteristic of the electron emission current Ie of the electron-emitting device shows Ie suddenly rising about half of the applied voltage (device voltage Vf), If having the characteristic similar to that of Ie, but having a sufficiently smaller value than Ie.

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Furthermore, Ie observed when the electronemitting member 4 is destroyed, etc. due to the local field concentration on the electron-emitting member 4 has not suddenly fluctuated.

FIG. 5A shows the Ie fluctuation when each of the devices A, B, and C according to the present embodiment produced in the same producing method is driven with Vf, Va, and H set constant. It proves that the three devices A, B, and C indicate small fluctuation, and have similar Ie values.

For comparison, FIG. 5B shows the fluctuation of Ie (emission current) when each of the devices D, E, and F produced in the same producing method except omitting the equalizing process (shown in FIG. 4D) by the electron-emitting member 4 is driven. In the device D, a sudden drop of Ie is observed in the driving period. In the device F, Ie is stepwise reduced, and indicates a saturation tendency at a certain value. Ie of the device E is stable.

Thus, without performing the "equalizing process", the characteristic of devices are unequal because the devices have different portions where an electric field easily concentrates due to different configurations of fibrous carbon which is an electron-emitting member.

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Listed below are examples of three devices (A, B, and C), and described below is an example of an equalizing process among a number of devices according to the present invention. FIG. 14 shows electron emission characteristics of different devices A to C before the "equalizing process".

In this example, the threshold V_{th3} of the electron emission is largest for the device C, and the threshold V_{th1} of the electron emission is smallest for the device A.

When the device A is driven with a pulse voltage under the condition of the above mentioned reactive gas, the mechanism of the above mentioned chemical etching of carbon suddenly reduces the electron emission current of the device A. The process is performed with the voltage applied to the device A gradually increased until the electron emission cannot be substantially detected when the threshold voltage (V_{th3}) of the device c is obtained. Similarly, the process is performed on the device B until the current value is reduced from the value indicated by the

point B.

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Thus, if the characteristic of each device is evaluated under the condition after the reactive gas has been evacuated, the electron emission characteristics of the devices A and B can substantially match the electron emission characteristic of the device C.

A preferable method as the "equalizing process" among a number of devices is described below. The preferable method comprising the steps of: find the electron-emitting device whose threshold voltage required to emit an electron is determined to be low with the characteristic of other devices, and then make the threshold voltages of the other devices becomes closer to the threshold of the device whose threshold voltage is determined to be low with the other devices.

An example of the method for performing the equalizing process on an electron source for which a plurality of electron-emitting devices are provided is described below by referring to FIG. 8 based on the above mentioned principle. In FIG. 8, reference numeral 81 denotes an electron source substrate, reference numeral 82 denotes X direction wiring, reference numeral 83 denotes Y direction wiring, reference numeral 84 denotes an electron-emitting device, and reference numeral 85 denotes a connection line.

X direction wiring 82 is formed by m pieces of wiring, that is, Dxl, Dx2, ..., Dxm, and can be configured by conductive metal, etc. formed in the vacuum evaporation method, the printing method, the spattering method, etc. The material, the film thickness, the width of the wiring can be appropriately designed.

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The Y direction wiring 83 is formed by n pieces of wiring, that is, Dy1, Dy2, ..., Dyn, which is similarly formed in the X direction wiring 82.

Among the m pieces of X direction wiring 82 and n pieces of Y direction wiring 83, an inter-layer insulation layers (not shown in the attached drawings) for separating them, which layers separate both electrically.

The inter-layer insulation layer not shown in the attached drawings is configured by SiO_2 , etc. formed in the vacuum evaporation method, the printing method, the spattering method, etc. For example, it is formed in a desired shape on all or a part of the electron source substrate 81 on which the X direction wiring 82 is arranged. Its film thickness, material, and producing method are appropriately designed to stand the potential difference at the crossing portion between the X direction wiring 82 and the Y direction wiring 83.

The X direction wiring 82 and the Y direction

wiring 83 are led as external terminals.

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A pair of electrodes (not shown in the attached drawings) forming the electron-emitting device 84 are electrically connected by m pieces of the X direction wiring 82, n pieces of the Y direction wiring 83, and the connection line 85 comprising conductive metal, etc.

When the number of rows in the X direction and the number of columns in the Y direction increase in the simple matrix as shown in FIG. 8, there occurs apparent distribution of the voltage applied to each device due to a drop of voltage if the "equalizing process" is collectively performed by selecting all of the electron-emitting devices 84 in the matrix. For example, it is desired that the "equalizing process" is performed with line (wiring) by line (wiring) or the "equalizing process" is performed with one by one (dot sequentially).

In this embodiment, an example of the equalizing process performed on all electron-emitting devices is described. However, the equalizing process can be performed not on all electron-emitting devices, but only on a desired electron-emitting device.

Before performing the equalizing process, it is desired that the electric characteristic of the electron-emitting device 84 is measured. It can be determined how the electric characteristic of each

electron-emitting device can be set based on the data obtained in the measurement. The electric characteristic to be measured (monitored) is obtained by measuring the current occurring when a predetermined voltage is applied to each electron-emitting device or between the electron-emitting device and the anode.

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A current occurring in an electron-emitting device can be a current flowing between an extraction electrode and a cathode electrode when a predetermined voltage is applied between the extraction electrode and the cathode electrode of each electron-emitting device. A current occurring between the anode electrode and the electron-emitting device can be a current detected when a current flowing to anode (emission current from the electron-emitting device) when a predetermined voltage is applied between the anode electrode and the electron-emitting device.

It is desired that the measurements of the electric characteristic are made on all electron-emitting devices. However, when the number of electron-emitting device increases, measurements can be made only on limited devices, and the "equalizing process" can be performed based on the measurement value.

To have the electric characteristics of all electron-emitting devices close to a predetermined value range based on the measured electric

characteristic, it is desired to perform the "equalizing process" on all electron-emitting devices. However, if the electric characteristics of devices are not quite different from each other, the "equalizing process" can be performed only on the electron-emitting device having the characteristic out of the desired range.

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Described below is the above mentioned method of sequentially equalizing lines. For example, the 10 "equalizing process" is performed by commonly connecting (for example, a GND connection) n pieces of Y direction wiring, that is, Dyl, Dy2, ..., Dyn, applying positive potential to the Y direction wiring to Dxl of the X direction wiring, and selecting the 15 electron-emitting device at the row Dxl (electronemitting device connected to the wiring of Dx1) 84. Then, a similar voltage is applied to Dx2, the electron-emitting device at the row Dx2 is selected, and the "equalizing process" is performed. Similarly. 20 the rows Dx3, Dx4, ..., Dxm are sequentially selected, and the equalizing process is performed in the X direction in a line sequence. Thus, the influence of a voltage drop can be reduced. In this embodiment, the "equalizing process" is performed on all electron-25 emitting devices connected to one piece of X direction wiring. However, the "equalizing process" can be performed on some of the electron-emitting devices

connected to one pieces of the X direction wiring.

That is, the "equalizing process" is not performed on all electron-emitting devices, but can be performed only on desired electron-emitting devices.

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Then, in the "equalizing process" sequentially performed one (device) by one (device), each device is selected using the above mentioned matrix wiring using the above mentioned matrix wiring so that it can be independently driven, and the electron-emitting device 84 can be individually equalized. In this method, there is no influence of a voltage drop, but the time required to perform the process is proportional to the number of the devices. Therefore, any of the line sequence process, the point sequence process, and a collective process can be performed depending on the size or the use of an electron source. Also in this method, the equalizing process is not performed on all electron-emitting devices, but is performed only on desired electron-emitting devices.

Described below is the image-forming apparatus configured using the electron source of the above mentioned simple matrix by referring to FIG. 9. FIG. 9 shows a type of an example of the display panel of the image-forming apparatus.

In FIG. 9, reference numeral 81 denotes an electron source substrate 81 for which a plurality of electron-emitting devices are provided, reference

numeral 91 denotes a rear plate to which the electron source substrate 81 is fixed, reference numeral 96 denotes a face plate in which a fluorescent film 94, a metal back 95, etc. are formed inside a glass substrate 93. Reference numeral 92 denotes a support frame to which the rear plate 91 and the face plate 96 are bonded using frit glass, etc. Reference numeral 97 denotes an envelope can be formed and sealed by baking at the temperature of 400 to 500°C for over 10 minutes in the vacuum or nitrogen.

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As described above, the envelope 97 comprises the face plate 96, the support frame 92, and the rear plate 91. Since the rear plate 91 is provided mainly to reinforce the strength of the electron source substrate 81, the separate rear plate 91 is not required if the electron source substrate 81 itself is strong enough. That is, the support frame 92 can be bonded directly to the electron source substrate 81 so that the face plate 96, the support frame 92, and the electron source substrate 81 can configure the envelope 97. On the other hand, a support unit, referred to as a spacer, not shown in the attached drawings can be provided between the face plate 96 and the rear plate 91 to configure the envelope 97 durable against the atmosphere.

Furthermore, the "equalizing process" of the electron-emitting member 4 according to the present

embodiment can be performed by introducing a reactive gas using a gas lead tube 98 after forming the envelope 97. The lead gas and the reaction product can be removed at any time by an evacuation tube 99.

The image-forming apparatus according to the present embodiment can also be used as an image-forming apparatus, etc. as a display device such as a device for a television broadcast, video conference system, a computer, etc. and an optical printer configured by a photosensitive drum, etc.

(Embodiments)

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Described below in detail are practical embodiments according to the present invention. (First Embodiment)

As the first embodiment of the present invention, an electron is emitted between the cathode electrode and the extraction electrode of the electron-emitting device under the condition of an O₂ gas, and the "equalizing process" is performed. FIGS. 1A to 1E show a method of producing an electron-emitting device according to the present embodiment. FIGS. 3A and 3B are a plan view and a sectional view of the produced electron-emitting device. Described below is the step of producing the electron-emitting device according to the present embodiment.

(Step 1 (FIG. 1A))

A quarts substrate is cleaned and used as the

substrate 1. 5 nm thick Ti and 30 nm thick Pt area are continuously evaporated in the spatter method as the extraction electrode 2 and the cathode electrode 3.

Then, in the photolithography process, a resist pattern is formed using a positive type photoresist (AZ 1500 made by Clariant).

Next, the Pt layer and Ti layer dry etching processes are performed using Ar with the patterned photoresist as a mask, and the extraction electrode 2 and the cathode electrode 3 having the gap of 5 μ m between the electrodes are formed.

(Step 2 (FIG. 1B))

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Then, about 100 mm thick Cr is piled in the evaporating process. In the photolithography process, a resist pattern is formed using a positive type photoresist (AZ 1500 made by Clariant).

Next, using the patterned photoresist as a mask, the area (100 μ m square) for coating the electronemitting member 4 is formed on the cathode electrode 3, and the Cr of an aperture is removed by a cerium nitrate etching solution.

After removing the photoresist, a complex solution obtained by adding a Pd complex to isopropyl alcohol, etc. is applied by a spin coat.

25 After the application, a heat treatment is performed at 300°C in the atmosphere, about 10 nm thick palladium oxide 41 is formed on the cathode electrode

3, and then Cr is removed by the cerium nitrate etching solution.

(Step 3 (FIG. 1C))

The atmosphere is evacuated with the heat of 200°C, the heat treatment is performed in the flow of the 2% hydrogen diluted by nitrogen. At this step, an about 3 to 10 nm diameter particle 42 is formed on the surface of the cathode electrode 3. At this time, the density of the particle 42 is estimated to be about 10^{11} to $10^{12}/\text{cm}^2$.

(Step 4 (FIG. 1D))

Then, in the flow of 0.1% ethylene diluted by nitrogen, the heat treatment is performed at 500°C for 10 minutes. When this process is observed by a scanning electronic microscope, it proves that a number of pieces of fibrous carbon 43 extending as 10 to 25 nm diameter curving fiber are formed on the Pd coated area. At this time, the fibrous carbon 43 is about 500 nm thick.

20 (Step 5 (FIG. 1E))

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Then, a device is provided in the vacuum device 20 shown in FIGS. 2A and 2B, the vacuum pump 23 performs the evacuation up to 1×10^{-5} Pa, the gas leading valve 22 leads an 0_2 gas until the vacuum level in the vacuum device 20 reaches 1×10^{-4} Pa, and a pulse voltage is applied to the cathode electrode 3 with the extraction electrode 2 set positive. The system is driven for 1

hour in this state, and the electron-emitting member 4 is equalized.

The electron-emitting device is formed in the above mentioned steps, and completely evacuated by the evacuation device 63 in the vacuum device 60 shown in FIG. 6 until 2 \times 10⁻⁶ Pa is reached, and an anode voltage Va = 10 kV is applied to the anode electrode 61 H = 2 mm apart as shown in FIG. 6.

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At this time, a pulse voltage of device voltage Vf = 20 V is applied to the electron-emitting device, and the flowing device current If and the electron emission current Ie are measured.

The Ie characteristic of the electron-emitting device shows a sudden increase of Ie from the half of the applied voltage, and the electron emission current Ie of about 1 μA is measured with Vf of 15 V. Thus, a preferable electron emission characteristic can be obtained with a small fluctuation of Ie with time.

On the other hand, If is similar to the characteristic of Ie, and the value is smaller than the value of Ie by one digit.

The mechanism of the equalizing process according to the present embodiment is described below by referring to FIG. 13. FIG. 13 shows a change in device characteristic before and after the equalizing process.

The electron-emitting device before the equalizing process shows the characteristic of emitting an

electron at the threshold V_{th1} (about 1 $V/\mu m$). Then, as described above, when a pulse voltage is applied to the device in the O_2 gas, the electron emission current of the device is suddenly reduced by the mechanism of the chemical etching of the above mentioned carbon. The voltage applied to the device is gradually increased, and the process is performed until no emission is emitted at the threshold voltage of V_{th2} .

When the device characteristic is evaluated after evacuating the $\rm O_2$ gas, the characteristic has been changed such that an electron is emitted at the threshold of $\rm V_{th2}$. At this time, it is assumed that the fluctuation width of the electron emission current obtained by the electron emission has been reduced, and the number of electron emission points has increased in the equalizing process.

The diameter of an electron beam emitted from the device obtained according to the present embodiment is long in the Y direction and short in the X direction, that is, substantially rectangular.

(Second Embodiment)

An example of the equalizing process performed by emitting an electron as biased between the cathode electrode of the electron-emitting device and the anode opposing the electron-emitting device in the ${\rm O_2}$ gas in the second embodiment.

(Step 1)

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In the method similarly used in the steps 1 to 4 according to the first embodiment, the extraction electrode 2 and the cathode electrode 3 are formed on the substrate 1, and fibrous carbon is produced as the electron-emitting member 4 on the substrate 1.

(Step 2)

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The electron-emitting device is provided for the vacuum device 20 as shown in FIGS. 2A and 2B, the evacuation device 23 performs the evacuation process until 2 \times 10⁻⁶ Pa is reached, the gas leading valve 22 leads the O_2 gas until the vacuum level in the vacuum device 20 reaches 1 \times 10⁻⁴ Pa, and the pulse voltage of Vf = 20 V (with the pulse width of 10 msec and the pulse length of 4 msec) is applied to the cathode electrode 3 of the electron-emitting device with the extraction electrode 2 of the electron-emitting device set positive. Simultaneously, a voltage of Va = 10 kV is applied to the anode 24. The system is operated in this state for 1 hour, and the electron-emitting member 4 is equalized.

The electron-emitting device produced as mentioned above is fixed to the Vr of 15 V, the inter-anode distance H is fixed to 2 mm, and the device is driven with the anode voltage Va of 10 kV. With the configuration, a stable Ie can be obtained as in the first embodiment.

(Third Embodiment)

An example of the equalizing process performed for each line of a matrix in the display device comprising a matrix electron source in which a plurality of electron-emitting devices are provided is described below by referring to FIGS. 8 and 9.

In FIG. 8, reference numeral 81 denotes an electron source substrate, reference numeral 82 is X direction wiring, and reference numeral 83 is Y direction wiring, reference numeral 84 denotes an electron-emitting device, and reference numeral 85 denotes a connection line.

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When the device capacity of a plurality of devices increases, the waveform becomes unclear by the capacity elements although a short pulse accompanied by the pulse width modulation is added in the matrix wiring as shown in FIG. 8, and the problem that an expected gray scale cannot be obtained, etc. occurs.

Therefore, according to the present embodiment as in the first embodiment, an inter-layer insulation layer is provided close to the electron-emitting member 4, thereby reducing the increase by the capacity element outside the element emission area.

In FIG. 8, the X direction wiring 82 comprises m pieces of wiring, that is, Dx1, Dx2, ..., Dxm, and comprises about 1 µm thick and 300 µm wide aluminum wiring material formed in the evaporation method. The material, thickness of film, and width of the wiring

are appropriately designed.

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The Y direction wiring 83 comprises n pieces of wiring, that is, Dyl, Dy2, ..., Dyn, and is 0.5 μ m thick and 100 μ m wide as similarly formed as the X direction wiring 82.

There is an inter-layer insulation layer not shown in the attached drawings between the m pieces of X direction wiring 82 and n pieces of Y direction wiring 83. They are electrically separated (m and n indicate positive integers).

The inter-layer insulation layer not shown in the attached drawings is configured by a 0.8 µm thick SiO₂ in the spatter method, etc. The thickness of the inter-layer insulation layer is determined such that it can be formed in a desired shape on all or a part of the substrate 81 forming the X direction wiring 82, specifically such that it is durable against the potential difference of the cross portion between the X direction wiring 82 and the Y direction wiring 83, that is, the device capacity per device is 1 pF or smaller, and the device durability of 30 V according to the present embodiment.

The X direction wiring 82 and the Y direction wiring 83 are lead as external terminals.

A pair of electrodes (not shown in the attached drawings) forming the electron-emitting device 84 electrically connected through m pieces of X direction

wiring 82, n pieces of Y direction wiring 83, and the connection line 85 comprising a conductive metal, etc.

According to the present embodiment, the Y direction wiring and the X direction wiring are connected respectively as the cathode electrode side and the extraction electrode side.

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The n pieces of Y direction wiring of Dy1, Dy2, ..., Dyn are commonly grounded, the pulse voltage on the positive side to the ground is applied to Dx1, the electron-emitting device 84 of the row Dx1 is selected, and the equalizing process is performed.

Then, a similar voltage is applied to Dx2, the electron-emitting device 84 of the row Dx2 is selected, and the equalizing process is performed. Similarly, the rows Dx3, Dx4, ..., Dxm are selected to perform the equalizing process sequentially in the X direction.

The image-forming apparatus configured using the electron source in the simple matrix array is described below by referring to FIG. 9. FIG. 9 shows the display panel of the image-forming apparatus using soda lime glass as a glass substrate material.

In FIG. 9, reference numeral 81 denotes an electron source substrate for which a plurality of electron-emitting devices are provided, reference numeral 91 denotes a rear plate to which the electron source substrate 81 is fixed, and reference numeral 96 denotes a face plate in which the fluorescent film 94,

the metal back 95, etc. are formed inside the glass substrate 93. Reference numeral 92 denotes a support frame to which the rear plate 91 and the face plate 96 are connected using frit glass, etc. Reference numeral 97 denotes an envelope which is sealed by baking at the temperature of 450°C in the vacuum for ten minutes.

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Reference numeral 84 denotes an electron-emitting device. X direction wiring 82 and Y direction wiring 83 are connected to a pair of device electrodes of an electron-emitting device. The respective row wiring and column wiring of the X direction wiring 82 and the Y direction wiring 83 are lead outside the envelope 97 as terminals of Doxl to Doxm and Doyl to Doyn.

The envelope 97 comprises the face plate 96, the support frame 92, and the rear plate 91 as described above. In the other hand, the envelope 97 having sufficient strength against the atmosphere by providing a support referred to as a spacer, but not shown in the attached drawings between the face plate 96 and the rear plate 91.

The metal back 95 performs a smoothing process (normally referred to as a "filming") on the inner surface of the fluorescent film 94 after producing the fluorescent film 94, and then the vacuum evaporation process, etc. is performed, thereby piling Al.

To enhance the conductivity of the fluorescent film 94, the face plate 96 is provided with a

transparent electrode (not shown in the attached drawings) outside the fluorescent film 94.

Since the electron from the electron source is emitted to the extraction electrode 2 side according to the present embodiment, the fluorescent film 94 is provided in the position 200 μm shifted toward the extraction electrode 2 when the anode voltage Va is 10 kV and the inter-anode distance H is 2 mm.

Thus, the obtained matrix electron source indicates equal characteristic for each electron-emitting device 84, and indicates little distribution of Ie, therefore it is desired as a display device, etc.

(Fourth Embodiment)

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According to the present embodiment, an example of an equalizing process is performed for each electron-emitting device in the display device as an image-forming apparatus comprising a matrix electron source for which a plurality of electron-emitting devices are provided.

As in the third embodiment, the matrix electron source as shown in FIG. 8 is produced. According to the present embodiment, the Y direction wiring 83 is connected to the cathode electrode, and the X direction wiring 82 is connected to the extraction electrode.

A voltage is applied to Dyl and Dxl, the electronemitting device 84 at the cross portion between Dyl and Dx1 is selected, and it is independently driven and the equalizing process is performed.

Then, a similar voltage is applied to Dy1 and Dx2, the electron-emitting device 84 at the cross portion between Dy1 and Dx2 is independently selected, and the equalizing process is performed. Similarly, the equalizing process is performed sequentially on each of the electron-emitting devices 84.

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Using the matrix electron source produced according to the present embodiment, the display device as shown in FIG. 9 is produced as in the third embodiment.

With the matrix electron source obtained as described above, the distribution of Ie is further reduced, and is recommended as a display device, etc.

As described above, according to the present invention, the shapes of a plurality of projections of the electron-emitting member 4 are equalized.

Therefore, a local field condensation is avoided on the electron-emitting member, and the electron emission

local field condensation which causes high current density and an overload can be suppressed, thereby avoiding the reduction of an emission current.

characteristic can be equalized. Additionally, the

Therefore, the induction of discharge can be suppressed, the durability of the electron-emitting device can be elongated, and a stable electron emission

current with a small fluctuation with time can be maintained for a long period.

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Furthermore, for an electron source and an imageforming apparatus provided with a plurality of
electron-emitting devices, the electron emission
current of each electron-emitting device can be stably
maintained. Therefore, the durability of each pixel
can be elongated, the brightness of an image can be
successfully represented, and the flicker of an image
can be avoided, thereby maintaining a constant display
characteristic for a long period.

WHAT IS CLAIMED IS:

- A method for producing an electron-emitting device, comprising the steps of:
- (A) disposing a cathode electrode on a surface of a substrate;
 - (B) providing an electrode opposite the cathode electrode;
 - (C) disposing plural pieces of fiber containing carbon as a main component on the cathode electrode; and
 - (D) applying potential higher than potential applied to the cathode electrode under depressurized condition to an electrode opposite the cathode electrode.

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2. The method for producing an electron-emitting device, according to claim 1, wherein

said electrode opposite the cathode electrode is an anode electrode provided apart the substrate.

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3. The method for producing an electron-emitting device, according to claim 1, wherein

said electrode opposite the cathode electrode is a leading electrode provided apart from the cathode electrode on the surface of the substrate.

4. The method for producing an electron-emitting

device, according to claim 1, wherein

said step of applying potential to the electrode opposite the cathode electrode is a step of increasing the number of emission sites.

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5. The method for producing an electron-emitting device, according to claim 1, wherein

said potential applied to the electrode opposite the cathode electrode is potential at which an electron is emitted from the fiber.

6. The method for producing an electron-emitting device, according to claim 1, wherein

said step of applying the potential to the electrode opposite the cathode electrode is performed under condition of a gas chemically or physically reactive to the fiber.

7. The method for producing an electron-emitting device, according to claim 6, wherein

said gas chemically reactive to the fiber is one of O_2 , H_2 , CO_2 , and H_2O .

8. The method for producing an electron-emitting device, according to claim 6, wherein

a pressure for introducing the gas is equal to or over 1 \times $10^{\text{-4}}$ Pa.

9. The method for producing an electron-emitting device, according to claim 6, wherein

said step of applying the potential to the electrode opposite the cathode electrode is a step of applying a pulse voltage between the cathode electrode and the electrode opposite the cathode electrode.

- 10. The method for producing an electron-emitting device, according to claim 1, wherein
- said fiber is formed by decomposing a hydrogen carbide gas.

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- 11. The method for producing an electron-emitting device, according to claim 10, wherein
- said fiber is formed by decomposing the hydrogen carbide gas using a catalyst provided on the cathode electrode in advance.
- 12. The method for producing an electron-emitting20 device, according to claim 11, wherein

said catalyst is one of Fe, Co, Pd, and Ni, or an alloy consisting of materials selected from among Fe, Co, Pd, and Ni.

25 13. The method for producing an electron-emitting device, according to claim 1, wherein

said fiber is formed by graphite nanofiber, carbon

nanotube, or amorphous carbon fiber.

14. The method for producing an electron-emitting device, according to claim 1, wherein

5 said fiber comprises a graphen.

15. The method for producing an electron-emitting device, according to claim 1, wherein

said fiber comprises a plurality of graphens.

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16. The method for producing an electron-emitting device, according to claim 15, wherein

said plurality of graphens are layered in an axial direction of the fiber.

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17. A method for producing an electron source obtained by arranging a plurality of electron-emitting devices, which are produced according to any of claims 1 to 16.

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18. A method for producing an image-forming apparatus having an electron source and an image-forming member, wherein

said electron source is produced in the method according to claim 17.

19. A method for producing an electron source

having a plurality of electron-emitting devices, comprising the steps of:

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- (A) providing on a substrate a plurality of electron-emitting devices comprising plural pieces of fiber each containing carbon as a main component, and plural pieces of wiring electrically connected to at least one of the plurality of electron-emitting devices;
- (B) measuring by applying a voltage to at least a part of the plurality of electron-emitting devices, an electrical characteristic of said at least a part of the plurality of electron-emitting devices to which the voltage is applied;
 - (C) reducing a difference in electrical characteristic among the plurality of electron-emitting devices based on a measurement result, wherein

said step of reducing the difference in characteristic among the plurality of electron-emitting devices comprising a step of emitting an electron from at least one of the plurality of electron-emitting devices under depressurized condition.

- 20. The method for producing an electron source, according to claim 19, wherein
- said plural pieces of wiring comprises plural pieces of row direction wiring, and plural pieces of column direction wiring crossing the row direction

wiring, and each of the electron-emitting devices is connected to one of the row direction wiring and one of the column direction wiring.

21. The method for producing an electron source, according to claim 20, wherein

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said step of reducing the difference in characteristic among the plurality of electron-emitting devices contains a step of emitting an electron from a desired electron-emitting device by repeating a step of selecting from said plural pieces of column direction wiring or said plural piece of row direction wiring, a part of the pieces of column direction wiring or row direction wiring, and emitting an electron from an electron-emitting device connected to the selected wiring.

- 22. The method for producing an electron source, according to claim 19, wherein
- 20 said step of reducing the difference in characteristic among the plurality of electron-emitting devices contains a step of emitting an electron from a desired electron-emitting device by repeating a step of selecting a part of electron-emitting devices from 25 among the plurality of electron-emitting devices and emitting an electron from the selected electron-emitting device.

23. The method for producing an electron source, according to claim 19, wherein:

said electron-emitting device contains a cathode electrode to which the fiber is electrically connected, and a leading electrode provided apart from the cathode electrode; and

said step of emitting an electron from the electron-emitting device is performed by applying a voltage between the cathode electrode and the leading electrode.

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24. The method for producing an electron source, according to claim 19, wherein

said step of emitting an electron from the electron-emitting device is performed by applying a voltage between the electrode provided apart from the substrate and the electron-emitting device.

25. The method for producing an electron source, according to claim 19, wherein:

said electron-emitting device contains a cathode electrode to which the fiber is electrically connected, and a leading electrode provided apart from the cathode electrode; and

25 said step of emitting an electron from the electron-emitting device is performed by applying a potential difference between an electrode provided

apart from the substrate and the electron-emitting device.

26. The method for producing an electron source,according to claim 19, wherein

said step of reducing the difference in characteristic among the plurality of electron-emitting devices is a step of increasing the number of emission sites of at least one electron-emitting device.

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27. The method for producing an electron source, according to claim 19, wherein

said step of reducing the difference in characteristic among the plurality of electron-emitting devices is performed in ambient of a gas chemically or physically reactive to the fiber.

- 28. The method for producing an electron source, according to claim 27, wherein
- said gas chemically reactive to the fiber contains a gas selected at least from among O_2 , H_2 , CO_2 , and H_2O .
 - 29. The method for producing an electron source, according to claim 28, wherein
- a pressure for introducing the gas is equal to or over 1 \times 10⁻⁴ Pa.

30. The method for producing an electron source, according to claim 27, wherein

said step of emitting an electron from the electron-emitting device is performed by applying a pulse voltage to the electron-emitting device.

31. The method for producing an electron source, according to claim 19, wherein

said fiber is formed by decomposing a hydrogen carbide gas.

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32. The method for producing an electron-emitting device, according to claim 31, wherein

said fiber is formed by decomposing the hydrogen carbide gas using a catalyst provided on the cathode electrode in advance.

- 33. The method for producing an electron-emitting device, according to claim 32, wherein
- said catalyst is one of Fe, Co, Pd, and Ni, or an alloy consisting of materials selected from among Fe, Co, Pd, and Ni.
- 34. The method for producing an electron-emitting25 device, according to claim 19, wherein

said fiber is formed by graphite nanofiber, carbon nanotube, or amorphous carbon fiber.

- 35. The method for producing an electron-emitting device, according to claim 19, wherein said fiber comprises a graphen.
- 5 36. The method for producing an electron-emitting device, according to claim 19, wherein said fiber comprises a plurality of graphens.
- 37. An electron-emitting device according to claim 36, wherein

said plurality of graphens are layered in an axial direction of the fiber containing carbon as a main component.

15 38. A method for producing an image-forming apparatus having an electron source and an electron-emitting member, wherein

said electron source is produced in the method according to any of claims 19 to 37.

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39. The method for producing an image-forming apparatus, according to claim 38, wherein

said image-forming apparatus is obtained by seal bonding a first substrate provided with the image-forming member with a second substrate provided with the electron source; and an electrical characteristic of the electron-emitting device is measured before the

first and second substrates are seal bonded with each other.

40. The method for producing an image-forming apparatus, according to claim 38, wherein

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said image-forming apparatus is obtained by seal bonding a first substrate provided with the image-forming member with a second substrate provided with the electron source; and said step of reducing the difference in electrical characteristic among the plurality of electron-emitting devices is performed before the first and second substrates are seal bonded with each other.

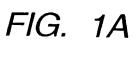
ABSTRACT OF THE DISCLOSURE

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A method for producing a durable electron-emitting device having a uniform electron emission characteristic, an electron source, and an image-forming apparatus having a uniform display characteristic for a long period are provided. The method for producing an electron-emitting device according to the present invention includes the steps of: disposing a cathode electrode on a surface of a substrate; providing an electrode opposite the cathode electrode; disposing plural pieces of fiber containing carbon as a main component on the cathode electrode; and applying potential higher than potential applied to the cathode electrode under depressurized condition to an electrode opposite the cathode electrode.



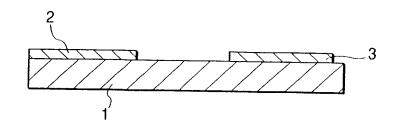


FIG. 1B

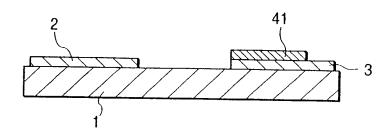


FIG. 1C

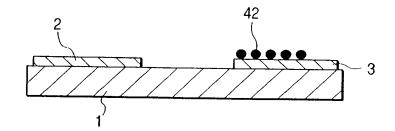


FIG. 1D

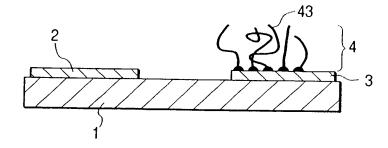


FIG. 1E

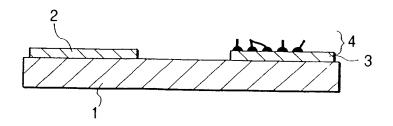


FIG. 2A

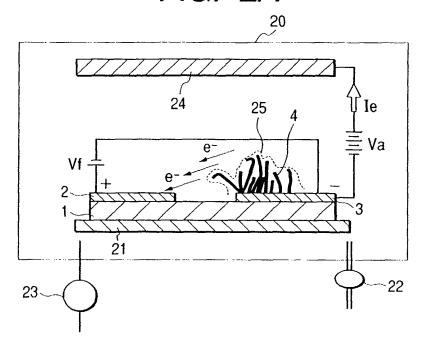


FIG. 2B

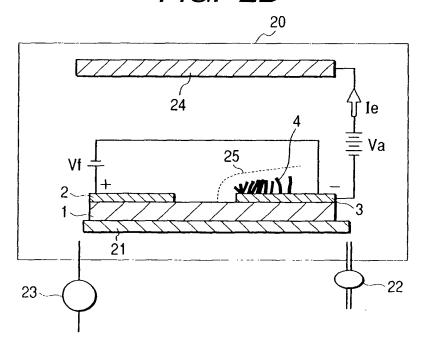
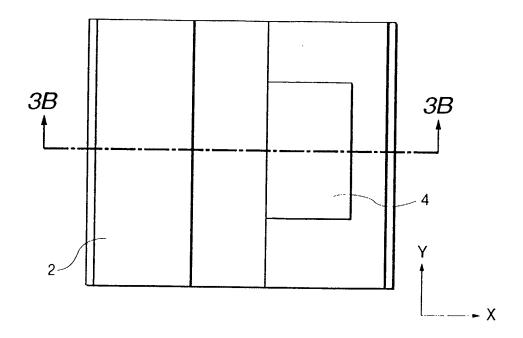


FIG. 3A



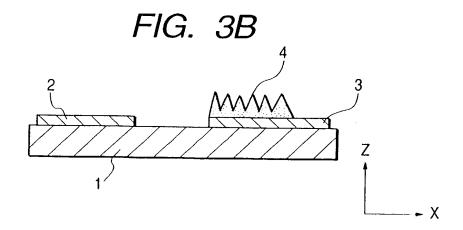


FIG. 4A

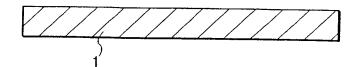


FIG. 4B

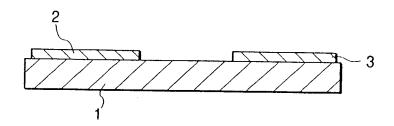


FIG. 4C

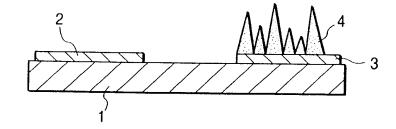


FIG. 4D

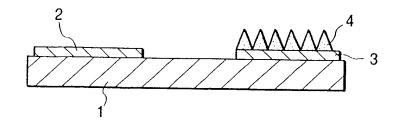


FIG. 5A

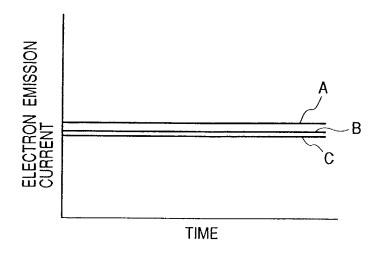


FIG. 5B

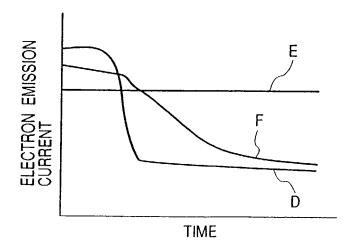


FIG. 6

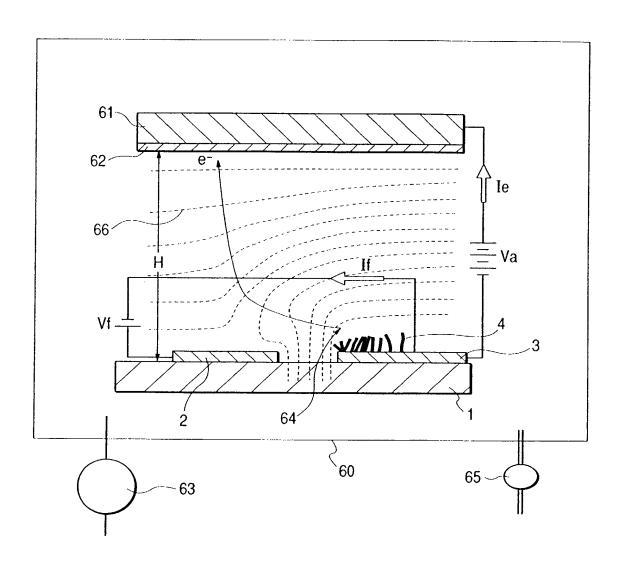


FIG. 7

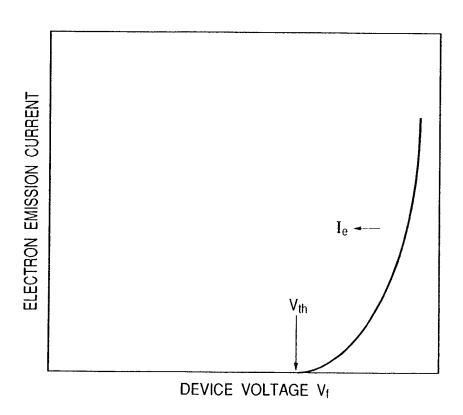
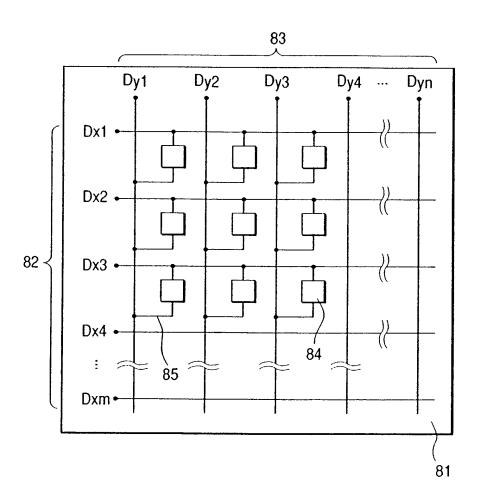


FIG. 8



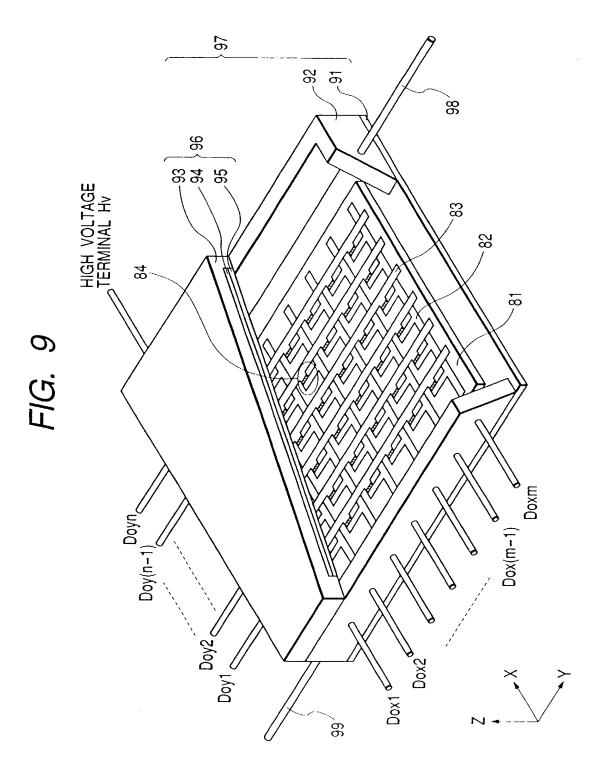


FIG. 10

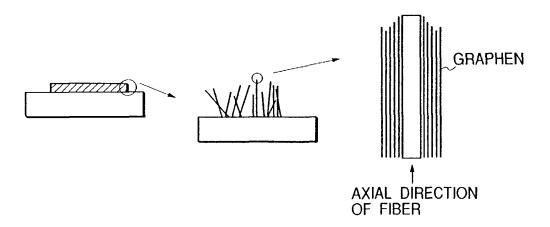


FIG. 11

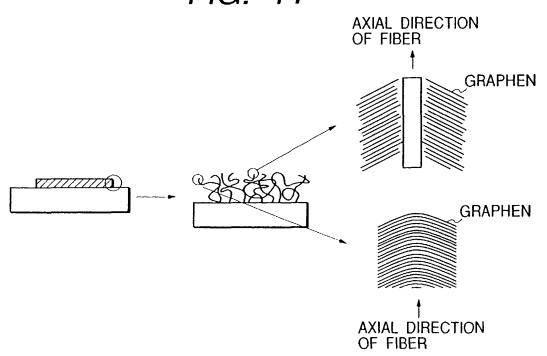


FIG. 12

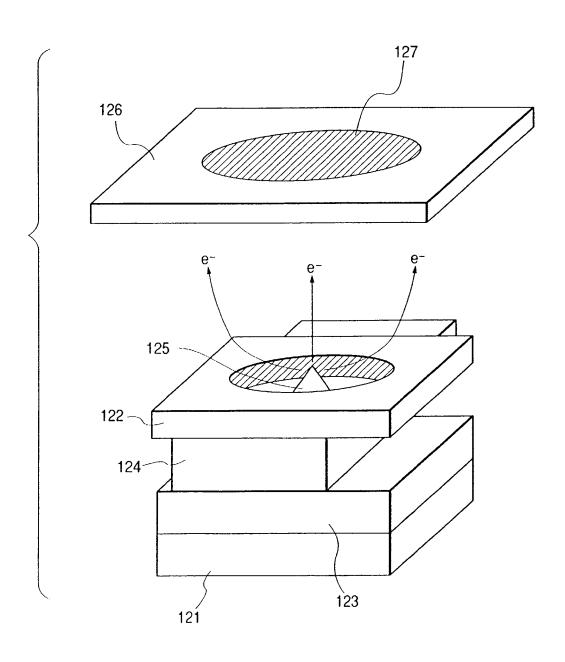


FIG. 13

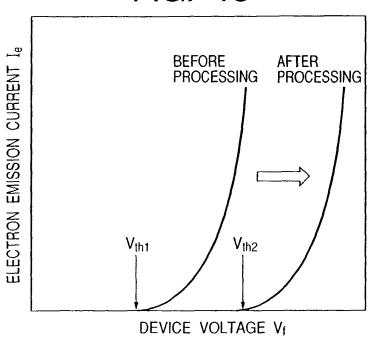
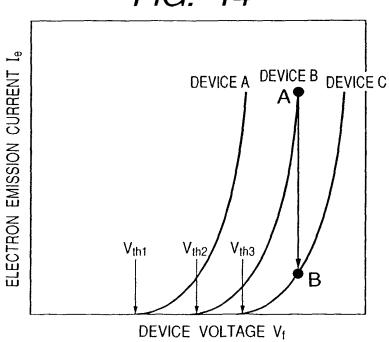


FIG. 14



CFO 9747 US



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Method of Manufacturing Electron-emitting Device
as well as Electron Source and Image-forming Apparatus

- 1 -

BACKGROUND OF THE INVENTION

Field of the Invention

This invention relates to a method of manufacturing an electron-emitting device and it also relates to an electron source and an image-forming apparatus such as a display apparatus incorporating an electron-emitting device manufactured by such a method.

Related Background Art

There have been known two types of electronemitting device; the thermoelectron type and the cold cathode type. Of these, the cold cathode type include the field emission type (hereinafter referred to as the FE-type), the metal/insulation lyaer/metal type (hereinafter referred to as the MIM-type) and the surface conduction type.

Examples of the FE electron-emitting device

20 are described in W. P. Dyke & W. W. Dolan, "Field
emission", Advance in Electron Physics, 8, 89 (1956)
and C. A. Spindt, "PHYSICAL Properties of thin-film
field emission cathodes with molybdenum cones", J.
Appl. Phys., 47, 5248 (1976).

25 MIM devices are disclosed in papers including C. A. Mead, "The tunnel-emission amplifier", J. Appl. Phys., 32, 646 (1961).

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Surface conduction electron-emitting devices are proposed in papers including M. I. Elinson, Radio Eng. Electron Phys., 10 (1965).

A surface conduction electron-emitting device is realized by utilizing the phenomenon that electrons are emitted out of a small thin film formed on a substrate when an electric current is forced to flow in parallel with the film surface. While Elinson proposes the use of SnO₂ thin film for a device of this type, the use of Au thin film is proposed in G. Dittmer: "Thin Solid Films", 9, 317 (1972) whereas the use of In_2O_3/SnO_2 and that of carbon thin film are discussed respectively in M. Hartwell and C. G. Fonstad: "IEEE Trans. ED Conf.", 519 (1975) and in H. Araki et al.: "Vacuum", Vol. 26, No. 1, p.22 (1983).

Fig. 24 of the accompanying drawings schematically illustrates a typical surface conduction electronemitting device proposed by M. Hartwell.

In Fig. 24, reference numeral 221 denotes a substrate. Reference numeral 224 denotes an electroconductive film normally prepared as integrally with a pair of device electrodes 225, 226 by producing an Hshaped metal oxide thin film by means of sputtering, part of which eventually makes an electron-emitting region 223 when it is subjected to an electrically 25 energizing process referred to as "electric forming" as described hereinafter. In Fig. 24, the horizontal area of the metal oxide thin film separating the

pair of device electrodes 225, 226 has a length L of 0.5 to 1.0 mm and a width W of 0.1 mm. Note that the electron-emitting region 223 is only very schematically shown because there is no way to accurately know its location and contour.

As described above, the electroconductive film 224 of such a surface conduction electron-emitting device is normally subjected to an electrically energizing preliminary process, which is referred to as "electric forming", to produce an electron emitting region 223.

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In the electric forming process, a DC voltage or a slowly rising voltage that rises typically at a rate of lV/min. is applied to given opposite ends of the electroconductive film 224 to partly destroy, deform or transform the thin film and produce an electron-emitting region 223 which is electrically highly resistive. Thus, the electron-emitting region 223 is part of the electronductive film 224 that typically contains fissures therein so that electrons may be emitted from those fissures. Note that, once subjected to an electric forming process, a surface conduction electron-emitting device comes to emit electrons from its electron emitting region 223 whenever an appropriate voltage is applied to the electroconductive film 224 to make an electric current run through the device.

Since a surface conduction electron-emitting device as described above is structurally simple and can be manufactured in a simple manner, a large number of such devices can advantageously be arranged on a large area without difficulty. As a matter of fact, a number of studies have been made to fully exploit this advantage of surface conduction electron-emitting devices. Applications of devices of the type under consideration include charged electron beam sources and electronic displays.

In typical examples of application involving a large number of surface conduction electron-emitting devices, the devices are arranged in parallel rows to show a ladder-like shape and each of the devices are respectively connected at given opposite ends with wirings (common wirings) that are arranged in columns to form an electron source (as disclosed in Japanese Patent Application Laid-open Nos. 64-31332, 1-283749 and 1-257552).

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As for display apparatuses and other imageforming apparatuses comprising surface conduction
electron-emitting devices such as electronic displays,
although flat-panel type displays comprising a liquid
crystal panel in place of a CRT have gained popularity
in recent years, such displays are not without
problems. One of the problems is that a light source
needs to be additionally incorporated into the display

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in order to illuminate the liquid crystal panel because the display is not of the so-called emission type and, therefore, the development of emission type display apparatuses has been eagerly expected in the industry.

An emission type electronic display that is free from this problem can be realized by using an electron source prepared by arranging a large number of surface conduction electron-emitting devices in combination with fluorescent bodies that are made to shed visible light by electrons emitted from the electron source (See, for example, United States Patent No. 5,066,883).

For a surface conduction electron-emitting device of the above described type, the electro-15 conductive film is desirably made of a metal oxide having an electric resistance sufficiently greater than that of a metal film as in the case of the above described M. Hartwell's electroconductive film 224 20 (Fig. 24). This is because a large electric current is required for the electric forming operation if the electroconductive film 224 has a low electric resistance when the electron-emitting region is produced by electric forming. The required electric 25 current will be huge and beyond any practical level particularly when a large number of surface conduction electron-emitting devices need to be simultaneously

subjected to an electric forming operation in the process of manufacturing an electron source comprising a plurality of surface conduction electron-emitting devices.

On the other hand, an electron source comprising a plurality of surface conduction electron-emitting devices and an image-forming apparatus incorporating such an electron source can be driven only by consuming electric power at an enhanced rate if the electroconductive film of each device has a high electric resistance.

SUMMARY OF THE INVENTION

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In view of the above identified technological problems, it is therefore an object of the present invention to provide a method of manufacturing an electron-emitting device that can effectively reduce the drive voltage and the power consumption level of the device.

Another object of the invention is to provide an electron source and an image-forming apparatus that operate on a power saving basis.

Still another object of the invention is to provide an electron source comprising a plurality of electron-emitting devices that operate uniformly for electron emission and an image-forming apparatus incorporating such an electron source and capable of

displaying high quality images.

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A further object of the present invention is to provide a method of manufacturing an electron-emitting device that can effectively reduce the electric current for electric forming and the, power consumption level required for driving the device as well as an energy saving electron source comprising a plurality of such electron-emitting devices that operate uniformly for electron emission and an image-forming apparatus incorporating such an electron source and capable of displaying high quality images.

According to a first aspect of the invention, the above objects and other objects of the invention are achieved by providing a method of manufacturing an electron-emitting device comprising a pair of oppositely disposed electrodes and an electroconductive film inclusive of an electron-emitting region arranged between said electrodes characterized in that said method comprises a processing step of reducing the electric resistance of the electroconductive film arranged between the electrodes.

Preferably, said processing step of reducing the electric resistance of the electroconductive film arranged between the electrodes is a step of chemically reducing the electroconductive film.

According to a second aspect of the invention, there is provided an electron source comprising an

electron-emitting device for emitting electrons as a function of input signals characterized in that said electron-emitting devices are produced by said manufacturing method.

According to a third aspect of the invention, there is provided an image-forming apparatus comprising an electron source and an image-forming member for forming images as a function of input signals characterized in that said electron source is an electron source comprising an electron-emitting device produced by said manufacturing method.

BRIEF DESCRIPTION OF THE DRAWINGS

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Fig. 1A shows a schematic plan view of a

5 surface conduction electron-emitting device produced
by a manufacturing method according to the invention
and Fig. 1B shows an equivalent circuit for driving
the device.

Fig. 2 is a graph showing the relationships

20 between the device current and the device voltage and
between the emission current and the device voltage
before and after the chemical reduction step of an
electron-emitting device being produced by a manufacturing method according to the invention.

25 Figs. 3A to 3C show schematic sectional views of an electron-emitting device in different steps of manufacturing by a method according to the invention.

Fig. 4 is a schematic diagram showing the configuration of a measuring system for determining the performance of an electron-emitting device.

Figs. 5A and 5B show forming voltage waveforms that can suitably be used for the purpose of 'the present invention.

Fig. 6 is a graph showing a typical relationships between the emission current Ie and the device voltage Vf and between the device current If and the device voltage Vf of a surface conduction electronemitting device produced by a manufacturing method according to the invention.

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Figs. 7A and 7B schematically show a plan view and a sectional view, respectively, of a surface conduction electron-emitting device produced by a manufacturing method according to the invention.

Fig. 8 schematically shows a sectional view of a surface conduction electron-emitting device of a type different from that of the device of Figs. 7A and 7B produced by a manufacturing method according to the invention.

Fig. 9 is a schematic plan view of an electron source having a simple matrix arrangement of electron-emitting devices.

Fig. 10 is a schematic perspective view of the display panel of an image-forming apparatus comprising an electron source having a simple matrix arrangement

l of electron-emitting devices.

Figs. 11A and 11B show two alternative fluorescent films that can be used for the purpose of the invention.

Fig. 12 is a block diagram of the drive circuit of an image-forming apparatus according to the invention adapted for the NTSC system.

Figs. 13A and 13B schematically show two alternative ladder-like arrangements of electronemitting devices for an electron source according to the invention.

Fig. 14 is a schematic perspective view of the display panel of an image-forming apparatus according to the invention incorporating an electron source

15 having a ladder-like arrangement of electron-emitting devices.

Fig. 15 is an enlarged schematic partial view of an electron source having a simple matrix arrangement of electron-emitting devices.

20 Fig. 16 is a schematic sectional view of an electron-emittnig device of the electron source of Fig. 15 taken along line A-A'.

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Figs. 17A to 17F and 18G to 18I show schematic sectional views of an electron-emitting device to be used for an electron source having a simple matrix arrangement, showing different manufacturing steps.

Fig. 19 is a schematic illustration of the

chemical reduction step of a method of manufacturing an electron-emitting device according to the invention, using a reducing gas.

Fig. 20 is a schematic sectional view of an electron-emitting device according to the invention after it is covered by a protective film.

Fig. 21 is a schematic illustration of the chemical reduction step of a method of manufacturing an electron-emitting device according to the invention and conducted in a reducing solution.

Fig. 22 is a block diagram of the drive circuit of an image-forming apparatus according to the invention adapted for the NTSC system obtained by modifying that of Fig. 12.

15 Fig. 23 is a block diagram of a display apparatus realized by using an image-forming apparatus according to the invention.

Fig. 24 is a schematic plan view of a conventional surface conduction electron-emitting device.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

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Now, the present invention will be described in greater detail by referring to the accompanying drawings.

25 According to an aspect of the invention, there is provided a method of manufacturing an electron-emitting device comprising an electroconductive film

- as a component thereof, wherein said method comprises
 a processing step of reducing the electric resistance
 of the electroconductive film so that the voltage to be
 applied to and the power consumed by the electron-
- 5 emitting device may be significantly reduced.

The processing step of reducing the electric resistance of the electroconductive film of an electron-emitting device will be described by referring to Figs. 1A, 1B and 2.

- 10 Fig. 1A shows a schematic plan view of a surface conduction electron-emitting device produced by a manufacturing method according to the invention and comprising a pair of electrodes 5, 6 and an electroconductive film 4 inclusive of an electron-emitting
- region 3 arranged between the electrodes. Note that reference numeral 1 denotes an insulating substrate and the electron-emitting region 3 contains fissures to make itself electrically highly resistive.

When a certain voltage is applied to the electroconductive film 4 by an external power source via the
electrodes 5, 6 to cause an electric current to flow
therethrough, the electron-emitting region 3 emits
electrons.

Fig. 1B shows an equivalent circuit for driving the electron-emitting device.

Referring to Fig. 1B, Rs and Rf respectively denote the electric resistance of the electron-emitting

region 3 and that of each of the oppositely arranged remaining portions of the electroconductive film 4.

While the oppositely disposed portions of the electroconductive film 4 other than the electron emitting region 3 may have different values for electric resistance from each other, it is assumed here for the same of convenience that the electron emitting region 3 is arranged exactly in the middle between the electrodes and the remaining portions of the electroconductive film 4 have electric resistances that are equal to each other.

If the electric current required to cause the electron-emitting device to emit electrons is id and the voltage required to be applied to the device in order to cause the current id to flow through the device is Vf, the power consumption rate P(all) of the electron-emitting device is expressed by equation P(all)=Vf·id.

effective power consumption rate Ps=Rs·id² that represents the power consumed per unit time genuinely by the electron emitting region in order to emit electrons and the ineffective power consumption rate Pf'=2·Rf'·id² that represents the power consumed per unit time by the remaining portions of the electroconductive film 4 that are connected in series to the electron emitting region 3.

While the above description concerns a single electron-emitting device, the overall ineffective power consumption rate would become enormous for an electron source comprising a plurality of such electron-emitting devices and hence for an image-forming apparatus incorporating such an electron source.

The drive voltage and the power consumption rate of the electron-emitting device can be reduced by reducing the ineffective power consumption rate Pf', that is, by making the electric resistance of the portions of the electroconductive film 4 Rf' (hereinafter referred to as the electric resistance of the electroconductive film 4) sufficiently small relative to the electric resistance of the electron emitting region 3 per se.

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If the electric resistance per unit square of the electroconductive film 4 is RoD, then the electric resistance of the electroconductive film 4 Rf' is expressed by Rf'=[L/(2·W)]·RoD. While Rf' can be made smaller by reducing the distance L between the electrodes 5 and 6 (hereinafter referred to as gas length), a small value for L is not desirable because it can seriously damage the flexibility with which the entire electron-emitting device is to be designed.

25 More specifically, for an image-forming apparatus having a large display screen, the distance L between the electrode 5 and 6 of each

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electron-emitting device of the apparatus is preferably not smaller than 3µm and more preferably not smaller than tens of several µm from the view point of the currently available level of performance of the 5 aligner, the accuracy of printing, the yield 'and other manufacturing considerations for patterning the electrodes.

In view of the above technological restrictions, the present invention is intended to provide a method of manufacturing a surface conduction electronemitting device comprising a pair of oppositely disposed electrodes and an electroconductive film inclusive of an electron-emitting region arranged between said electrodes characterized in that said 15 method comprises a processing step of reducing the electric resistance of the electroconductive film arranged between the electrodes.

Preferably, said processing step of reducing the electric resistance of the electroconductive film arranged between the electrodes is a step of chemically reducing the electroconductive film. With such an operation of chemically reducing the electroconductive film 4, the ineffective power consumption rate Pf' of the electroconductive film 4 can be 25 significantly reduced to allow electric power to be effectively consumed for electron emission in the device.

current If and the device voltage Vf and between the emission current Ie and the device voltage Vf before and after the chemical reduction step of an electron-emitting device being produced by a manufacturing method according to the invention will be described schematically by referring to Fig. 2. In Fig. 2, the device current and the emission current before chemical reduction are respectively indicated by Ifo and Ieo whereas those after chemical reduction are respectively denoted by Ifm and Iem.

As clearly seen from Fig. 2, both Ifo and Ieo before chemical reduction are smaller than their respective counter-parts Ifm and Iem after chemical reduction. This means that almost all the device voltage Vf applied to the electron-emitting device is applied to the electron emitting region after the operation of chemical reduction, whereas the device voltage Vf is significantly lowered by the resistance of the electroconductive film and only a fraction of the device voltage Vf is actually applied to the electron emitting region before the chemical reductions step. In other words, a higher device voltage needs to be applied to the electron-emitting device before the chemical reduction step in order to compensate the loss in the electroconductive film if an emission current level equal to the level after the chemical

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reduction step is to be achieved before the chemical reduction step in the electron-emitting device. Then, electric power will be consumed by the electroconductive film at an even higher rate.

Thus, according to the invention, the power consumption rate of an electron-emitting device can be reduced by chemically reducing the electroconductive film. Preferable techniques for chemically reducing the electroconductive film for the purpose of the present invention include 1) heating the film in vacuum, 2) keeping the film in an reducing atmosphere and 3) keeping the film in a reducing solution. With any of these techniques, the operation of chemically reducing the electroconductive film is conducted, while monitoring the electric resistance of the electroconductive film, until the resistance gets to a stable level and does not become lower any further.

Now, the best mode of carrying out the invention will be described.

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Firstly, a method of manufacturing a surface conduction electron-emitting device according to the invention will be described by referring to Figs. 3A-3C that show a surface conduction electron-emitting device in three different manufacturing steps.

A method of manufacturing a surface conduction electron-emitting device according to the invention comprises the following steps.

- 1 (A) Steps upto electric forming: the electroconductive film arranged between a pair of electrodes on a substrate is subjected to an electric forming operation.
 - 1) After thoroughly cleansing a substrate 1 with
- detergent and pure water, a material is deposited on the substrate 1 by means of vacuum deposition, sputtering or some other appropriate technique for a pair of device electrodes 5 and 6, which are then produced by photolithography (Fig. 3A).
- 2) An organic metal thin film is formed on the substrate 1 between the pair of device electrodes 5 and 6 by applying an organic metal solution and leaving the applied solution for a given period of time. Thereafter, the organic metal thin film is
- heated in an oxidizing atmosphere, for instance, in the ambient air atmosphere and is charged to an electroconductive film which comprises mainly metal oxides and subsequently subjected to a patterning operation, using an appropriate technique such as
- 20 lift-off or etching, to produce a thin film 2 for forming an electron-emitting region (Fig. 3B). While an organic metal solution is used to produce a thin film in the above description, a thin film may alternatively be formed by vacuum deposition,
- sputtering, chemical vapor phase deposition, dispersed application, dipping, spinner or some other technique.
 - 3) Thereafter, the device is subjected to an electric

forming process.

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In this electric forming operation, the electroconductive film 4 is locally destroyed, deformed or transformed such that a portion of the electroconductive film 4 undergoes a structural change (to become a high electric resistance area) as fissures are formed there. Differently stated, a portion of the electroconductive film 4 undergoes a structural change to make an electron emitting region 3 in an electric forming process where a voltage is applied to the device electrodes 5 and 6 by a power source (not shown) to energize the electroconductive film 4 (Fig. 3C).

All the remaining steps of the electric

15 processing to be conducted on the device after the forming operation are carried out by using a measuring system which will be described below by referring to Fig. 4.

Referring to Fig. 4, the measuring system

20 comprises a power source 31 for applying a voltage to
the device, an ammeter 30 for metering the device
current If running through the electroconductive film
4 between the device electrodes, an anode 34 for
capturing the emission current Ie emitted from the

25 electron-emitting region 3 of the device, a high
voltage source 33 for applying a voltage to the anode
34 of the measuring system, another ammeter 32 for

metering the emission current Ie emitted from the electron-emitting region 3 of the device, a vacuum apparatus 35 and an exhaust pump 36. The exhaust pump may be provided with an ordinary high vacuum system comprising a turbo pump and a rotary pump or'an oil-free high vacuum system comprising an oil-free pump such as a magnetic levitation turbo pump or a dry pump and an ultra-high vacuum system comprising an ion pump.

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An electron-emitting device is placed in the vacuum apparatus 35 for carrying out the remaining steps of electric processing or for measuring the performance of the device, which comprises a substrate 1, a pair of device electrodes 5 and 6 and an electroconductive film 4 including an electron emitting region 3 as shown in Fig. 4.

The vacuum apparatus 35 is provided with a vacuum gauge and other pieces of equipment necessary to operate it so that the measuring operation can be conducted under a desired vacuum condition.

The vacuum chamber and the substrate of the electron source can be heated to approximately 400°C by means of a heater (not shown).

For determining the performance of the device,

25 a voltage between 1 and 10KV is applied to the anode,
which is spaced apart from the electron emitting device
by distance H which is between 2 and 8mm.

1 For the electric forming operation, a constant pulse voltage or an increasing pulse voltage may be applied. Figs. 5A and 5B show two possible electric forming voltage waveforms.

5 For the purpose of the present invention, the voltage to be applied to the device for an electric forming operation preferably have a pulse waveform. Fig. 5A shows a constant pulse waveform where the pulse wave height is constant, whereas Fig. 5B shows an 10 increasing pulse waveform where the pulse wave height increases with time.

Firstly, a voltage having a constant pulse wave height will be described by referring to Fig. 5A.

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Referring to Fig. 5A, the pulse voltage has a pulse width Tl and a pulse interval T2, which are between 1 microsecond and 10 microseconds and between 10 microseconds and 100 milliseconds respectively. The height of the triangular wave (the peak voltage for the electric forming operation) may be appropriately 20 selected depending on the profile of the electronemitting device to be processed and the voltage is applied for several seconds to several tens of minutes under an appropriate vacuum conditions, for instance, typically with a degree of vacuum of approximately 10⁻⁵torr. Note that the pulse waveform to be applied to the device electrodes is not limited to a triangular waveform and may alternatively be a rectangular

waveform or some other appropriate waveform.

the device in vacuum.

deform the thin film.

Secondly, a voltage having an increasing waveform will be described by referring to Fig. 5B.

Referring to Fig. 5B, the pulse voltage has a width Tl and a pulse interval T2, which are between 1 microsecond and 10 microseconds and between 10 microseconds and 100 milliseconds respectively as in the case of Fig. 5A, although the height of the triangular wave (the peak voltage for the electric 10 forming operation) is increased at a rate of, for instance, 0.1V per step and the voltage is applied to

The electric forming operation will be terminated when typically a resistance greater than 15 lM ohms is observed for the device current If running through the electroconductive thin film 4 for forming an electron-emitting region while applying a resistancemeasuring voltage of approximately 0.1V is applied to the device electrodes not to locally destroy or 20

- (B) Reduction of electric resistance: the electroconductive film arranged between a pair of electrodes is subjected to a processing operation of reducing the electric resistance thereof.
- 25 4) The processing operation of reducing the electric resistance of the electroconductive film is an operation of chemically reducing the electroconductive

1 film.

The processing operation of chemically reducing the electroconductive film 4 including an electronemitting region 3 arranged between a pair of device electrodes 5 and 6 on a substrate 1 is conducted in a manner as described below. In this operation, a monitoring device that has been subjected only to steps 1) and 2) of (A) and not to the electric forming operation is preferably used along with the device to 10 be processed so that the end of the operation of chemically reducing the electroconductive film 4 of the device may be determined by observing changes in the resistance of the electroconductive film 4 of the monitoring device that has not been electrically formed 15 and is concurrently subjected to the operation of chemical reduction.

Techniques that can be used for chemically reducing the electroconductive film 4 include the following.

20 (1) heating the film in vacuum

The heating temperature for this technique is preferably between 100°C and 400°C, although it depends on the degree of vacuum involved and the components of the electroconductive film.

25 (2) keeping the film in a reducing atmosphere

Gaseous substances that can be used for this
technique include hydrogen, hydrogen sulfide, hydrogen

- iodide, carbon monoxide, sulfur dioxide and other lower gaseous oxides. The heating temperature for this technique is preferably between room temperature (20°C) and 400°C, although it depends on the gaseous substance involved.
 - (3) keeping the film in a reducing solution

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Reducing solutions that can be used for this technique include solutions of hydrazine, diimides, formic acid, aldehydes and L-ascorbic acid. The heating temperature for this technique is preferably between 20°C and 100°C.

- 5) The device that has undergone the above steps is then subjected to an activation step which will be described below.
- In this activation step, a pulse voltage having a constant wave height is repeatedly applied to the device in vacuum of a degree typically between 10⁻⁴ and 10⁻⁵torr as in the case of the forming operation so that carbon or carbon compounds may be deposited on the device out of the organic substances existing in the vacuum in order to cause the device current If and the emission current Ie of the device to change markedly and obtain an electron-emitting device having a high emission current Ie and a high electron emission

The carbon or carbon compounds as referred to above are found to be mostly graphite (both mono- and

poly-crystalline) and non-crystalline carbon (or a mixture of amorphous carbon and poly-crystalline graphite) if observed through a TEM or a Raman spectroscopes and the thickness of the film deposited is preferably less than 500 angstroms and more preferably less than 300 angstroms.

For the purpose of the present invention, the activation step preferably precedes the chemical reduction step.

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More specifically, the electroconductive film 4 may show deformation on the surface due to agglomeration in the course of the chemical reduction process to make the electron-emitting region 3 partly short-circuited depending on the components of the electroconductive film 4 and/or the conditions for the operation of chemical reduction. Once such a short-circuited state takes place, the device current If can be increased to consequently reduce the ratio of the electron emission current Ie to the device current If.

The reduction in the ratio of the electron emission current Ie to the device current If can be prevented by forming a coating film on the electroconductive film 4 at a location near the electronemitting region 3 at the time of deposition of carbon or carbon compounds in the activation step in order to suppress any possible agglomeration and consequent

1 deformation of the electroconductive film 4 in the succeeding chemical reduction step.
6) The prepared electron-emitting device is preferably driving to operate in vacuum of a degree higher than
5 those of the electric forming step and the activation steps. Preferably, the device is heated at 80°C to 150°C in vacuum of such a high degree. The degree of vacuum higher than those of the electric forming step and the activation step typically means a vacuum of
10 not higher than 10⁻⁶torr and, preferably an ultra-high vacuum state under which carbon and carbon compounds

Thus, any additional deposition of carbon and/or carbon compounds is suppressed to stabilize both the
15 device current If and the emission current Ie.

would not be additionally deposited.

Now, some of the basic features of an electron-emitting device according to the invention and prepared in the above described manner will be described below by referring to Fig. 6.

20 Fig. 6 shows a graph schematically illustrating the relationship between the device voltage Vf and the emission current Ie and between the device voltage Vf and the device current If typically observed by the measuring system of Fig. 4. Note that different units 25 are arbitrarily selected for Ie and If in Fig. 6 in view of the fact that Ie has a magnitude by far smaller than that of If.

As seen in Fig. 6, an electron-emitting device according to the invention has three remarkable features in terms of emission current Ie, which will be described below.

Firstly, an electron-emitting device according to the invention shows a sudden and sharp increase in the emission current Ie when the voltage applied thereto exceeds a certain level (which is referred to as a threshold voltage hereinafter and indicated by Vth in Fig. 6), whereas the emission current Ie is practically undetectable when the applied voltage is found lower than the threshold value Vth. Differently stated, an electron-emitting device according to the invention is a non-linear device having a clear threshold voltage Vth to the emission current Ie.

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Secondly, since the emission current Ie is highly dependent on the device voltage Vf, the former can be effectively controlled by way of the latter.

20 Thirdly, the emitted electric charge captured by the anode 34 is a function of the duration of time of application of the device voltage Vf. In other words, the amount of electric charge captured by the anode 34 can be effectively controlled by way of the 25 time during which the device voltage Vf is applied.

Note that the device current If either monotonically increases relative to the device voltage

- 1 Vf (as shown by a solid line in Fig. 6, a characteristic referred to as MI characteristic hereinafter) or changes to show a form specific to a voltage-controllednegative-resistance characteristic (as shown by a broken
- line in Fig. 6, a characteristic referred to as VCNR characteristic hereinafter). These characteristics of the device current are dependent on a number of factors including the manufacturing method, the conditions where it is measured and the environment for operating the device. The MI characteristic is preferably used for the purpose of the present invention.

Now, a flat type surface conduction electronemitting device will be described.

Figs. 7A and 7B respectively show a schematic

15 plan view and a schematic sectional view of a surface conduction electron-emitting device produced by a manufacturing method according to the invention.

Referring to Figs. 7A and 7B, the device comprises a substrate 1, a pair of device electrodes 5 and 6, a

20 thin film 4 including an electron-emitting region 3.

Materials that can be used for the substrate 1 include quartz glass, glass containing impurities such as Na to a reduced concentration level, soda lime glass, glass substrate realized by forming an SiO₂ layer on soda lime glass by means of sputtering, ceramic

soda lime glass by means of sputtering, ceramic substances such as alumina.

While the oppositely arranged device electrodes

5 and 6 may be made of any highly conducting material, preferred candidate materials include metals such as Ni, Cr, Au, Mo, W, Pt, Ti, Al, Cu and Pd and their alloys, printable conducting materials made of a metal or a metal oxide selected from Pd, Ag, 'RuO₂, Pd-Ag and glass, transparent electroconductive materials such as In₂O₃-SnO₂ and semiconductor materials such as polysilicon.

the length W of the device electrodes, the contour of the electroconductive film 4 and other factors for designing a surface conduction electron-emitting device according to the invention may be determined depending on the application of the device. The distance L is preferably between several hundreds angstroms and several hundreds micrometers and, still preferably, between several micrometers and tens of several micrometers depending on the voltage to be applied to the device electrodes and the field strength available for electron emission.

The electroconductive thin film 4 is preferably a fine particle film in order to provide excellent electron-emitting characteristics. The thickness of the electroconductive thin film 4 is determined as a function of the stepped coverage of the thin film on the device electrodes 5 and 6, the electric resistance between the device electrodes 5 and 6 and the

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parameters for the forming operation that will be described later as well as other factors and preferably between several angstroms and several thousands angstroms and more preferably between ten angstroms and five hundreds angstroms.

The electroconductive film 4 is typically made of fine particles of a material selected from metals such as Pd, Ru, Ag, Ti, In, Cu, Cr, Fe, Zn, Sn, W and Pb after processed in the above described chemical reduction step, although it may contain oxides of those metals such as PdO, SnO₂, In₂O₃, PbO, MoO and MoO₂.

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The term "a fine particle film" as used herein refers to a thin film constituted of a large number of fine particles that may be loosely dispersed,

15 tightly arranged or mutually and randomly overlapping (to form an island structure under certain conditions).

The diameter of fine particles to be used for the purpose of the present invention is between several angstroms and several thousands angstroms and preferably between ten angstroms and two hundreds angstroms.

The electron-emitting region 3 is part of the electroconductive thin film 4 and comprises electrically highly resistive fissures, although its profile is dependent on the thickness and the material of the electroconductive thin film 4 and the electric forming process described earlier. It may contain electroconductive fine particles having a diameter

between several angstroms and hundreds of several angstroms. The material of such fine particles may be formed of all or part of the materials that are used to prepare the electroconductive thin film 4. The selectroconductive thin film 4 preferably contains

carbon and carbon compounds in the electron-emitting region 3 and its neighboring areas.

Now, a step type surface conduction electronemitting device, will be described.

10 Fig. 8 is a schematic sectional view of a step type surface conduction electron-emitting device, showing its basic configuration. The components same as or similar to those of the device of Figs. 7A and 7B are respectively denoted by the same reference symbols.

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The device comprises a substrate 1, a pair of device electrodes 5 and 6 and a electroconductive film 4 including an electron emitting region 3, which are made of materials same as a flat type surface conduction electron-emitting device as described above, as well as a step-forming section 21 made of an insulating material such as SiO₂ produced by vacuum deposition, printing or sputtering and having a film thickness corresponding to the distance L separating the device electrodes of a flat type surface conduction electron-emitting device as described above, or between several hundreds angstroms and tens of several micrometers and preferably between several hundreds angstroms and several micrometers, although it is selected as a

function of the method of producing the step-forming section used there, the voltage to be applied to the device electrodes and the field strength available for electron emission.

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As the electroconductive film 4 is formed after the device electrodes 5 and 6 and the step-forming section 21, it may preferably be laid on the device electrodes 5 and 6. The location and contour of the electro-emitting region 3 are dependent on the conditions under which it is prepared, electric forming conditions and other related conditions and not limited to the location and contour shown in Fig. 8.

Since an electron-emitting device produced by

15 a method according to the invention is provided with
the above described three remarkable features, its
electron-emitting performance can be easily and
accurately controlled as a function of input signals
even if it is used as one of a plurality of identical

20 electron-emitting devices comprised in an electron
source or an image-forming apparatus incorporating
such an electron source.

Then, an electron source and an image-forming apparatus comprising electron-emitting devices produced

by a manufacturing method according to the invention will be described in terms of their respective basic configurations.

1 An electron source and an image-forming apparatus can be realized by arranging a plurality of electron-emitting devices on a substrate. Electronemitting devices may be arranged on a substrate in a number of different modes. For instance, a number of 5 surface conduction electron-emitting devices as described earlier may be arranged in rows along a direction (hereinafter referred to row-direction), each device being connected by wirings at opposite 10 ends thereof, and driven to operate by control electrodes (hereinafer referred to as grids or modulation means) arranged in a space above the electron-emitting devices along a direction perpendicular to the row direction (hereinafter referred 15 to as column-direction) or, alternatively as described below, a total of m X-directional wirings and a total of n Y-directional wirings are arranged with an interlayer insulation layer disposed between the Xdirectional wirings and the Y-directional wirings along with a number of surface conduction electron-emitting devices such that the pair of device electrodes of each surface conduction electron-emitting device are connected respectively to one of the X-directional wirings and one of the Y-directional wirings. The latter arrangement is referred to as a simple matrix arrangement.

Now, the simple matrix arrangement will be

described in detail.

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In view of the three basic features of a surface conduction electron-emitting device according to the invention, each of the surface conduction electron-emitting devices in a configuration of simple matrix arrangement can be controlled for electron emission by controlling the wave height and the pulse width of the pulse voltage applied to the opposite electrodes of the device above the threshold voltage level. On the other hand, the device does not emit any electron below the threshold voltage level. Therefore, in the case of a number of electronemitting devices, desired surface conduction electronemitting devices can be selected and controlled for electron emission in response to the input signal by applying a pulse voltage to each of the selected devices.

Fig. 9 is a schematic plan view of the substrate of an electron source according to the invention

20 realized by using the above features. In Fig. 9, the electron source comprises a substrate 91 carrying a plurality of surface conduction electron-emitting devices arranged thereon (hereinafter referred to a electron source substrate), X-directional wirings 92,

25 Y-directional wirings 93, surface conduction electron-emitting devices 94 and connecting wires 95. The surface conduction electron-emitting devices may be

either of the flat type or of the step type. In Fig. 9, the electron source substrate 91 may be a glass substrate and the number and configuration of the surface conduction electron-emitting devices arranged on the substrate may be appropriately determined depending on the application of the electron source.

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There are provided a total of m X-directional wirings 92, which are donated by DX1, DX2, ..., DXm and made of an electroconductive metal formed by vacuum deposition, printing or sputtering. These wirings are so designed in terms of material, thickness and width that a substantially equal voltage may be applied to the surface conduction electron-emitting devices. A total of n Y-directional wirings are arranged and donated by DY1, DY2, ..., DYn, which are similar to the X-directional wirings 92 interms of material, thickness and width. An interlayer insulation layer (not shown) is disposed between the m X-directional wirings 92 and the n Y-directional 20 wirings 93 to electrically isolate them from each other, the m X-directional wirings and n Y-directional wirings forming a matrix. Note that m and n are integers.

The interlayer insulation layer (not shown) is 25 typically made of SiO₂ and formed on the entire surface or part of the surface of the insulating substrate 91 to show a desired contour by means of vacuum

- deposition, printing or sputtering. The thickness, material and manufacturing method of the interlayer insulation layer are so selected as to make it withstand any potential difference between an X-
- at the crossing thereof. Each of the X-directional wiring 93 wirings 92 and the Y-directional wirings 93 is drawn out to form an external terminal.

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The oppositely arranged electrodes (not shown) of each of the surface conduction electron-emitting devices 94 are connected to the related one of the m X-directional wirings 92 and the related one of the n Y-directional wirings 93 by respective connecting wires 95 which are made of an electroconductive metal and formed by vacuum deposition, printing or sputtering.

The electroconductive metal material of the device electrodes and that of the connecting wires 95 extending from the m X-directional wirings 92 and the n Y-directional wirings 93 may be same or contain common elements are components, the latter being appropriately selected depending on the former. If the device electrodes and the connecting wires are made of a same material, they may be collectively called device electrodes without discriminating the connecting wires. The surface conduction electron-emitting devices may be arranged directly on the substrate 91 or on the interlayer insulation layer (not shown).

1 As will be described in greater detail
hereinafter, the X-directional wirings 92 are
electrically connected to a scan signal generating
means (not shown) for applying a scan signal to a
5 selected row of surface conduction electron-emitting
devices 94 and scanning the selected row according to
an input signal.

On the other hand, the Y-directional wirings
93 are electrically connected to a modulation signal
generating means (not shown) for applying a modulation
signal to a selected column of surface conduction
electron-emitting devices 94 and modulating the
selected column according to an input signal.

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Note that the drive signal to be applied to

15 each surface conduction electron-emitting device is
expressed as the voltage difference of the scan
signal and the modulation signal applied to the
device.

With the arrangement of simple matrix wiring as described above, an electron source according to the invention can selectively and independently drive individual electron-emitting devices.

Now, an image-forming apparatus according to the invention and comprising an electron source having a simple matrix arrangement as described above will be described by referring to Figs. 10, 11A, 11B and 12. This apparatus may be a display apparatus.

Fig. 10 illustrates the basic configuration of the display panel of the image-forming apparatus and Figs. 11A and 11B show two alternative fluorescent films that can be used for the purpose of the invention, while Fig. 12 is a block diagram of the drive circuit of the image-forming apparatus which is adapted for the NTSC system.

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Referring firstly to Fig. 10, the apparatus comprises an electron source substrate 91 of the above described type, a rear plate 101 rigidly holding the electron source substrate 91, a face plate 106 produced by laying a fluorescent film 104 and a metal back 105 on the inner surface of a glass substrate 103 and a support frame 102. An envelope 108 is formed for the apparatus as frit glass is applied to said rear plate 101, said support frame 102 and said face plate 106, which are subsequently baked to 400 to 500°C in the atmosphere or in nitrogen and bonded together to a hermetically sealed condition.

In Fig. 10, reference numeral 94 denotes the electron-emitting region of each electron-emitting device as illustrated in Fig. 9 and reference numerals 92 and 93 respectively denotes the X-directional wiring and the Y-directional wiring connected to the respective device electrodes of each electron-emitting device.

While the envelope 108 is formed of the face

plate 106, the support frame 102 and the rear plate 101 in the above description, the rear plate 101 may be omitted if the substrate 91 is strong enough by itself because the rear plate 101 is provided mainly for reinforcement. If such is the case, an independent rear plate 101 may not be required and the substrate 91 may be directly bonded to the support frame 102 so that the envelope 108 is constituted of a face plate 106, a support frame 102 and a substrate 101. The overall strength against the atmospheric pressure of the envelope 108 may be increased by arranging a number of support members called spacers (not shown) between the face plate 106 and the rear plate 101.

possible arrangements of fluorescent bodies to form a fluorescent film 104. While the fluorescent film 104 comprises only fluorescent bodies if the display panel is used for showing black and white pictures, it needs to comprise for displaying color pictures black conductive members 111 and fluorescent bodies 112, of which the former are referred to as black stripes or members of a black matrix depending on the arrangement of the fluorescent bodies. Black stripes or members of a black matrix are arranged for a color display panel so that the fluorescent bodies 112 of three different primary colors are made less discriminable and the adverse effect of reducing the contrast of

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displayed images of external light is weakened by blackening the surrounding areas. While carbon black is normally used as a principal ingredient of the black stripes, other conductive material having low light transmissivity and reflectivity may alternatively be used.

A precipitation or printing technique may suitably be used for applying a fluorescent material on the glass substrate 103 regardless of black and white or color display.

An ordinary metal back 105 is arranged on the inner surface of the fluorescent film 104. The metal back 105 is provided in order to enhance the luminance of the display panel by causing the rays of light emitted from the fluorescent bodies and directed to the inside of the envelope to turn back toward the face plate 106, to use it as an electrode for applying an accelerating voltage to electron beams and to protect the fluorescent bodies against damages that may be caused when negative ions generated inside the envelope collide with them. It is prepared by smoothing the inner surface of the fluorescent film 104 (in an operation normally called "filming") and forming an Al film thereon by vacuum deposition after forming the fluorescent film 104.

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A transparent electrode (not shown) may be formed on the face plate 106 facing the outer surface

of the fluorescent film 104 in order to raise the conductivity of the fluorescent film 104.

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Care should be taken to accurately align each set of color fluorescent bodies and an electron-emitting device, if a color display is involved, before the above listed components of the enclosure are bonded together.

an exhaust pipe (not shown) to a degree of vacuum of approximately 10^{-7} torr and hermetically sealed. A getter operation may be carried out after sealing the envelope 108 in order to maintain that degree of vacuum in it. A getter operation is an operation of heating a getter (not shown) arranged at a given location in the envelope 108 immediately before or after sealing the envelope 108 by resistance heating or high frequency heating to produce a vapor deposition film. A getter normally contains Ba as a principle ingredient and the formed vapor deposition film can typically maintain the inside of the enclosure to a degree of 1×10^{-5} to 10^{-7} torr by its adsorption effect.

Fig. 12 shows a block diagram of the drive circuit for driving the display panel of an image-forming apparatus comprising an electron source having a simple matrix arrangement as described above, said apparatus being designed for image display operation using NTSC television signals.

In Fig. 12, reference numeral 121 denotes the display panel. The circuit further comprises a scan circuit 122, a control circuit 123, a shift register 124, a line memory 125, a synchronizing signal separation circuit 126, a modulation signal generator 127 and a pair of DC voltage sources Vx and Va.

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Each component of the apparatus operates in a manner as described below. The display panel 121 is connected to external circuits via terminals Doxl through Doxm, Doyl through Doym and a high voltage terminal Hv, of which terminals Doxl through Doxm are designed to receive scan signals for sequentially driving on a one-by-one basis the rows (of a total of N devices) of surface conduction electron-emitting devices arranged in the form of a matrix having M rows and N columns in the electron source. On the other hand, terminals Doyl through Doyn are designed to receive a modulation signal for controlling the output electron beam of each of the surface-conduction type electron-emitting devices of a row selected by a scan signal. High voltage terminal Hv is fed by the DC voltage source Va with a DC voltage of a level typically around 10kV, which is sufficiently high to energize the fluorescent bodies of the selected surface-conduction type electron-emitting devices.

The scan circuit 122 operates in a manner as follows.

The scan circuit 122 comprises M switching devices (which are schematically shown and denoted by symbols S1 and Sm in Fig. 12), each of which takes either the output voltage of the DC voltage source Vx or OV (the ground potential) and comes to be connected with one of the terminals Doxl through Doxm of the display panel 121. Each of the switching devices S1 through Sm operates in accordance with control signal Tscan fed from the control circuit 123 and can be easily prepared by combining transistors such as FETs.

The DC voltage source Vx of this mode of carrying out the invention is designed to output a constant voltage taking the characteristic properties (including the threshold voltage for electron emission) of the surface conduction electron-emitting devices into consideration.

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The control circuit 123 coordinates the operations of related components so that images may be appropriately displayed in accordance with externally fed picture signals. It generates control signals Tscan, Tsft and Tmry for the related components in response to synchronizing signal Tsync fed from the synchronizing signal separation circuit 126. These control signals will be described later in greater detail hereinafter.

The synchronizing signal separation circuit 126 separates the synchronizing signal component and the

luminance signal component from an externally fed NTSC television signal and can be easily realized using a popularly known frequency separation (filter) circuit. Although a synchronizing signal extracted from a

separation circuit 126 is constituted, as well known, of a vertical synchronizing signal and a horizontal synchronizing signal and a horizontal synchronizing signal, it is simply designated as Tsync signal here for convenience sake, disregarding its component signals. On the other hand, a luminance signal drawn from a television signal, which is fed to the shift register 124, is designed as DATA signal.

The shift register 124 carries out for each line a serial/parallel conversion on DATA signals that are serially fed on a time series basis in accordance with control signal Tsft fed from the control circuit 123. In other words, a control signal Tsft operates as a shift clock for the shift register 124. A set of data for a line that have undergone a serial/parallel conversion (and correspond to a set of drive data for N electron-emitting devices) are sent out of the shift register 124 as n parallel signals Idl through Idn.

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The line memory 125 is a memory for storing

25 a set of data for a line, which are signals Idl
through Idn, for a required period of time according
to control signal Tmry coming from the control circuit

1 123. The stored data are sent out as I'd1 through I'dn and fed to modulation signal generator 127.

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The modulation signal generator 127 is in fact a signal source that appropriately drives and modulates the operation of each of the surface-conduction type electron-emitting devices according to each of the picture data I'dl through D'dn and output signals of this device are fed to the surface-conduction type electron-emitting devices in the display panel 121 via terminals Doyl through Doyn.

As described above, an electron-emitting devices according to the present invention is characterized by the following features in terms of emission current Ie. There exists a clear threshold voltage Vth and the electron-emitting devices emit substantially no electron when a voltage that falls short of the threshold voltage Vth is applied thereto.

On the other hand, when the voltage applied to the surface conduction electron-emitting devices exceeds the threshold level, the rate of electron emission of the surface conduction electron-emitting devices varies as a function of the voltage applied thereto. While the threshold voltage Vth for electron emission and the rate of electron emission relative to the applied voltage may vary depending on the materials, the configuration and the manufacturing method of electron-emitting devices, the following

statement always holds true.

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When a pulse-shaped voltage is applied to an electron-emitting device according to the invention, it emits substantially no electron if the applied voltage is found below the threshold voltage, for electron emission but starts emitting electrons once the applied voltage exceeds the threshold level. Thus, firstly the rate of electron beam emission of the device can be controlled by appropriately changing the wave height, or amplitude Vm, of the pulse-shaped voltage. Secondly, the total electric charge of the electron beams being emitted by the device can be controlled by appropriately changing the pulse width Pw of the applied voltage.

Therefore, the electron-emitting device can be modulated as a function of input signals either by voltage modulation or by pulse width modulation.

The modulation signal generator 127 to be used for voltage modulation may comprise a circuit that generates a voltage pulse having a constant width and a variable wave height that varies as a function of input data.

On the other hand, the modulation signal generator 127 to be used for pulse width modulation comprises a circuit for generating a voltage pulse having a constant wave height and a variable pulse width that varies as a function of input data.

As a result of coordinated operation of the above described components, television images are displayed on the display panel 121 of the apparatus. Although it is not particularly mentioned above that the shift register 124 and the line memory 125 may be either of digital or of analog signal type so long as serial/parallel conversions and storage of video signals are conducted at a given rate.

If digital signal type devices are used, output
signal DATA of the synchronizing signal separation
circuit 126 needs to be digitized. However, such
conversion can be easily carried out by arranging an
A/D converter at the output of the synchronizing signal
separation circuit 126. In connection with this, it
should be noted that the circuit to be used for the
modulation signal generator 127 may have to be slightly
modified depending on if digital or analog signals are
produced by the line memory 125.

More specifically, when digital signals are used for voltage modulation, the modulation signal generator 127 may suitably comprise a D/A conversion circuit, to which an amplifying circuit may appropriately be added if necessary. For pulse width modulation, the modulation signal generator 127 may use a circuit typically comprising in combination a high speed oscillator, a counter for counting the number of waves produced by the oscillator and a comparator for

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comparing the output value of said counter and that of said memory. If necessary, an amplifier may additionally be used to amplify the voltage of the modulation signal produced by the comparator and modulated for pulse width to the level of the drive voltage of the surface conduction electron-emitting device.

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When, on the other hand, analog signals are used for voltage modulation, the modulation signal generator 127 may suitably comprise an amplifying circuit involving an operational amplifier and a level shift circuit may appropriately be added thereto if necessary. For pulse width modulation, the modulation signal generator 127 may comprise a voltage control type oscillation circuit (VCO), to which an amplifier may be added to amplify the voltage of the modulation signal to the level of the drive voltage of the surface conduction electron-emitting device.

with an image-forming apparatus according to

the invention and having a configuration as described above, the electron-emitting devices are selectively caused to emit electrons by applying a device voltage to them via the terminals Doxl through Doxm and Doyl through Doyn that are external to the envelope while applying a high voltage to the metal back 105 or the transparent electrode (not shown) via the high voltage terminal Hv in order to accelerate the emitted electron

beams until they collide with an energize the fluorescent film 104 so that the latter emits light and display images.

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While the configuration of an image-forming apparatus according to the invention is schematically described above, the materials and details of the components are not limited to the above description and may be modified appropriately depending on the application of the apparatus. While the present invention 10 is described above in terms of television image display using the NTSC television signal system, the TV signal system to be used is not limited to a particular one and any other system such as PAL or SECAM may feasibly be used with it. An image-forming apparatus according to the invention is particularly suited for TV signals involving a larger number of scanning lines typically of a high definition TV system such as the MUSE system because it can be used for a large display panel comprising a large number of scanning lines.

Now, an electron source having a ladder-like arrangement and an image-forming apparatus comprising such an electron source will be described for basic configuration by referring to Figs. 13A, 13B and 14.

Referring to Figs. 13A and 13B showing two
25 alternative ladder-like arrangements of electronemitting devices for an electron source, the electron
source comprises an electron source substrate 144, a

number of electron-emitting devices 131 and paired common wirings Dx1 through Dx10 collectively denoted by 132 for wiring the electron-emitting devices. The electron-emitting devices 131 are arranged in a plurality of parallel rows running along the'Xdirection on the substrate 144 (hereinafter referred to device rows).

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With such an arrangement, the device rows of the electron source can be independently driven by applying a drive voltage to the common wiring pairs (Dx1-Dx2, Dx3-Dx4, Dx5-DX6, Dx7-Dx8, Dx9-Dx10).

In other words, a voltage higher than the threshold voltage is applied to one or more than one device rows that have to emit electron beams whereas a voltage lower than the threshold level is applied to the remaining device rows that are not expected to emit electron beams. Alternatively, a single common wiring may be used for any two adjacent device rows (and common wirings Dx2 and Dx3, Dx4 and Dx5, Dx6 and Dx7 and Dx8 and Dx9 may be replaced by respective single common wirings).

Fig. 14 is a schematic perspective view of the display panel of an image-forming apparatus according to the invention incorporating an electron source having a ladder-like arrangement of electron-emitting devices. In Fig. 14, the display panel comprises grid electrodes 140, each provided with a number of through

- bores 141 for allowing electrons to pass therethrough, external terminals Doxl, Dox2, ..., Doxm collectively denoted by 142, external terminals G1, G2, ..., Gn collectively denoted by 143 and connected to the
- 5 respective grid electrodes and an electron source substrate 144 as shown in Fig. 13B. Note that the same components are respectively denoted by the same reference symbols in Figs. 13A, 13B and 14.

The display panel of Fig. 14 remarkably

differs from that of the image-forming apparatus of
Fig. 10 having a simple matrix arrangement in that it
additionally comprises grid electrodes 140 arranged
between the electron source substrate 144 and the face
plate 106.

15 As described above, strip-shaped grid electrodes 140 are arranged between the substrate 144 and the face plate 106 in Fig. 14 and rectangularly relative to the devices rows arranged in a ladder-like manner in such a way that they can modulate electron beams emitted 20 from the surface conduction electron-emitting devices of the electron source. The grid electrodes are provided with circular through bores 141 that are as many as the electron-emitting devices to make one-toone correspondence. However, the profile and the 25 location of the grid electrodes are not limited to those of Fig. 14 and may be modified appropriately so long as they are arranged near or around the electronemitting devices. Likewise, the through bores 141 may be replaced by meshes or the like.

The external terminals 142 and the external terminals for the grids 143 are electrically connected to a control circuit (not shown).

An image-forming apparatus having a configuration as described above can control the fluorescent film for electron beam irradiation by simultaneously applying modulatin signals to the columns of grid electrodes for a single line of an image in synchronism with driving the electron-emitting devices on a row by row basis so that the image can be displayed on a line by line basis.

Thus, a display apparatus according to the invention and having a configuration as described above can have a wide variety of industrial and commercial applications because it can operate as a display apparatus for television broadcasting, as a terminal apparatus for video teleconferencing and as an optical printer if it is combined with a photosensing drum.

[Examples]

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Now, the present invention will be described in greater detail by way of examples.

25 (Example 1)

The method of manufacturing electron-emitting devices will be described below in terms of an

1 experiment conducted on specimens, referring to Figs.
7A and 7B and Figs. 3A to 3C.
Step a:

plate a silicon oxide film was formed thereon'to a thickness of 0.5 microns by sputtering to produce a substrate 1, on which a pattern of photoresist (RD-2000N-41: available from Hitachi Chemical Co., Ltd.) was formed for a pair of device electrodes and a gap separating the electrodes and then Ti and Ni were sequentially deposited thereon respectively to thicknesses of 50Å and 1,000Å by vacuum deposition. The photoresist pattern was dissolved in an organic solvent and the Ni/Ti deposit film was treated by using a lift-off technique to produce a pair of device electrodes 5 and 6 having a width W of 300 microns and separated from each other by a distance L of 20 microns (Fig. 3A).

Step b:

A mask having opening for the gap L separating the device electrodes and its vicinity was used to form a Cr film to a film thickness of 1,000Å by vacuum deposition, which was then subjected to a patterning operation. Thereafter, organic Pd (ccp4230: available from Okuno Pharmaceutical Co., Ltd.) was applied to the Cr film by means of a spinner, while rotating the film, and baked at 300°C for 10 minutes to produce an

electroconductive film for forming an electron-emitting region, which was made of fine particles containing PdOx as a principal ingredient and had a film thickness of 100 angstroms and an electric resistance per unit area of $5 \times 10^4 \Omega/\Box$.

Note that the term "a fine particle film" as used herein refers to a thin film constituted of a large number of fine particles that may be loosely dispersed, tightly arranged or mutually and randomly overlapping (to form an island structure under certain conditions). The diameter of fine particles to be used for the purpose of the present invention is that of recognizable fine particles arranged in any of the above described states.

15 Step c:

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The Cr film and the baked electroconductive film for forming an electron-emitting region were etched by using an acidic etchant to produce an electroconductive film 4 having a desired pattern (Fig. 3B).

Now, a device having a pair of device electrodes and an electroconductive film disposed between the electrodes on the substrate was prepared. Step d:

25 Then, the substrate of the device was set in position in a gauging system as illustrated in Fig. 4 and the inside of the vacuum chamber of the system was

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evacuated by means of an exhaust pump to a degree of vacuum of 1x10⁻⁶torr. Subsequently, a voltage Vf was applied for 60 seconds from the power source 31 to the device electrodes 5, 6 to electrically energize the device (electric forming process) and produce a locally deformed (fissured) section (electron emitting region) 3 in the electroconductive film (Fig. 3C).

Fig. 5B shows the voltage waveform used for the electric forming process.

In Fig. 5B, T1 and T2 respectively denote the pulse width and the pulse interval of the applied pulse voltage, which were respectively 1 millisecond and 10 milliseconds for this example. The wave height (the peak voltage for the forming operation) of the applied pulse voltage was increased stepwise with steps of 0.1V.

It was found that fine particles containing palladium oxide as a principal ingredient were dispersed in the electron emitting region 3 of the device produced by following the above steps, the average diameter of the particles being 30 angstroms. Step e:

Subsequently, the electroconductive film 4 of the device that had undergone an electric forming operation was subjected to a chemical reduction process.

In this process, the device and a monitoring device that had not been processed for electric forming

1 (but had undergone the steps of through c above) were arranged in an apparatus having a configuration as shown in Fig. 4 and then heated to 130°C to 200°C for approximately 10 hours, while keeping the inside of the apparatus to a degree of vacuum of 1x10⁻⁶torr.

After the chemical reduction process, it was found that the electroconductive film containing PdOx as a principal ingredient of the monitoring device without an electric forming process had been chemically reduced to become a film of fine particles of Pd metal having an electric resistance per unit area of 5×10^2 Ω/Ω or a value smaller than the resistance before the chemical reduction by two digits.

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In an attempt to see the properties of the electron-emitting device prepared throughout the preceding steps, it was observed for electron-emitting performance, using a measuring system as illustrated in Fig. 4. In the above observation, the distance H between the anode 34 and the electron-emitting device was 4mm and the potential of the anode 34 was lkV, while the degree of vacuum in the vacuum chamber of the system was held to 1×10^{-6} torr throughout the gauging operation.

A device voltage was applied between the

device electrodes 5, 6 of the device to see the device
current If and the emission current Ie under that
condition. Fig. 6 shows the current-voltage

relationships obtained as a result of the observation.

An emission current Ie began to flow through the device immediately when the device voltage (Vf) became as high as 8V and a device current If of 3.0 mA and an emission current of 1.5 microA were observed when the device voltage rose to 14V to provide an electron emission efficiency n = Ie/Ifx100(%) of 0.05%.

When the devcie was observed before the chemical reduction process, the film of PdO fine particles (electroconductive film) of the device showed an electric resistance of $3.5k\Omega$ and the fissured area had an electric resistance of 4.7k Ω . After the chemical reduction process, it was found that the electric resistance of the film of PdO fine 15 particles of the electron-emitting device was as low as $35\,\Omega$, which was negligible when compared with that of the fissured area.

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In other words, for an electron-emitting device after a chemical reduction process according to the 20 invention to obtain the same electron emission rate as a device before the process having required a device voltage of 24.6V, the device after the process required a power consumption rate of only 42 milliW whereas it was 73.8 milliW for the device before the process, i.e. the former being 57% of the latter, thus proving a significant saving of power. (Example 2)

1 This example relates to an electron source comprising a plurality of electron-emitting devices produced by the method of Example 1 and an imageforming apparatus incorporating such an electron 5 source.

Fig. 15 shows a schematic partial plan view of the electron source and Fig. 16 shows a schematic partial sectional view taken along line A-A' of Fig. 15, while Figs. 17A to 17F and 18G to 18I illustrate schematic partial sectional views of the electron source shown in different manufacturing steps. Note that same or similar components are respectively designated by same reference symbols throughout Figs. 15 through 18I.

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91 denotes a substrate and 92 and 93 respectively denote X- and Y-directional wirings (which may be called lower and upper wirings respectively) that correspond to Dxm and Dyn in Fig. 9. Otherwise, the electron source comprises electron-20 emitting devices, each having an electroconductive film 4 and a pair of device electrodes 5 and 6, an interlayer insulation layer 161 and a number of contact holes, each of which is used to connect a device electrode 5 with a related lower wiring 92.

25 Now, the steps of manufacturing an electron source and an image-forming apparatus incorporating such as electron source used in this example will be described in detail.
Step a:

After thoroughly cleansing a soda lime glass

plate a silicon oxide film was formed thereon, to a

5 thickness of 0.5 microns by sputtering to produce a

substrate 91, on which Cr and Au were sequentially

laid to thicknesses of 50 angstroms and 6,000

angstroms respectively and then a photoresist

(AZ1370: available from Hoechst Corporation) was formed

10 thereon by means of a spinner, while rotating the film,

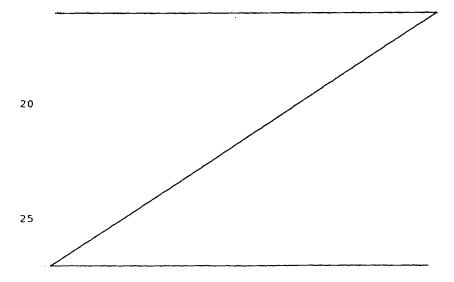
and baked. Thereafter, a photo-mask image was exposed

to light and developed to produce a resist pattern for

the lower wirings 92 and then the deposited Au/Cr film

was wet-etched to produce lower wirings 92 having a

desired profile (Fig. 17A).



1 Step b:

A silicon oxide film was formed as an interlayer insulation layer 161 to a thickness of 1.0 micron by RF sputtering (Fig. 17B).

5 Step c:

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A photoresist pattern was prepared for producing contact holes 162 in the silicon oxide film deposited in Step b, which contact holes 162 were then actually formed by etching the interlayer insulation layer 161, using the photoresist pattern for a mask (Fig. 17C).

RIE (Reactive Ion Etching) using ${\rm CF}_4$ and ${\rm H}_2$ gas was employed for the etching operation. Step d:

Thereafter, a pattern of photoresist (RD-2000N-41:

available from Hitachi Chemical Co., Ltd.) was formed for pairs of device electrodes 5 and 6 and gaps L1 separating the respective pairs of electrodes and then Ti and Ni were sequentially deposited thereon respectively to thicknesses of 50 Å and 1,000 Å by vacuum deposition.

The photoresist pattern was dissolved by an organic solvent and the Ni/Ti deposit film was treated by using a lift-off technique to produce pairs of device electrodes 5 and 6, each pair having a width of 300 microns and separated from each other by a distance L1 of 20 microns (Fig. 17D).

Step e:

After forming a photoresist pattern on the device

electrodes 5, 6 for upper wirings 93, Ti and Au were sequentially deposited by vacuum deposition to respective thicknesses of 50 angstroms and 5,000 angstroms and then unnecessary areas were removed by means of a lift-off technique to produde upper wirings 93 having a desired profile (Fig. 17E).

Step f:

A mask was prepared for the electroconductive $\tilde{\ }$ films 2 of the devices.

10 The mask had an opening for the gap L1 separating the device electrodes and its vicinity of each device. The mask was used to form a Cr film 171 to a film thickness of 1,000 Å by vacuum deposition, which was then subjected to a patterning operation.

15 Thereafter, organic Pd (ccp4230: available from Okuno

Pharmaceutical Co., Ltd.) was applied to the Cr film by means of a spinner, while rotating the film, and baked at 300°C for 10 minutes (Fig. 17F).

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The formed electroconductive films 2 were made of fine particles containing PdOx as a principal ingredient and had a film thickness of 100 angstroms and an electric resistance per unit area of 5 x 10^4 Ω/\Box .

Note that the term "a fine particle film" as used herein refers to a thin film constituted of a

25 large number of fine particles that may be loosely dispersed, tightly arranged or mutually and randomly overlapping (to form an island structure under certain

conditions). The diameter of fine particles to be used for the purpose of the present invention is that of recognizable fine particles arranged in any of the above described states.

5 Step g:

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The Cr film 171 and the baked electroconductive film 2 were etched by using an acidic etchant to produce a desired pattern (Fig. 18G).

Then, a pattern for applying photoresist to the entire surface area except the contact holes 162 was prepared and Ti and Au were sequentially deposited by vacuum deposition to respective thicknesses of 50 angstroms and 5,000 angstroms. Any unnecessary areas

were removed by means of a lift-off technique to consequently bury the contact holes 162 (Fig. 18H).

Now, lower wirings 92, an interlayer insulation layer 161, upper wirings 93, and devices comprising pairs of device electrodes 5 and 6 and electroconductive films 2 were produced on the substrate 91.

Then, an electron source comprising the above electron source substrate and an image-forming apparatus incorporating such an electron source were prepared. This will be described below by referring to Figs. 10, 11A and 11B.

The substrate 91 carrying thereon a large number of devices prepared according to the above described

process was rigidly fitted to a rear plate 101 and thereafter a face plate 106 (prepared by forming a fluorescent film 104 and a metal back 105 on a glass substrate 103) was arranged 5 mm above the substrate 91 by interposing a support frame 102 therebetween. Frit glass was applied to junction areas of the face plate 106, the support frame 102 and the rear plate 101, which were then baked at 400°C for 15 minutes in the atmosphere and bonded together to a hermetically sealed condition (Fig. 10). The substrate 91 was also firmly bonded to the rear plate 101 by means of frit glass.

In Fig. 10, reference numerals 92 and 93 respectively denote X- and Y-directional wirings.

made of fluorescent bodies if the image-forming apparatus is for black and white pictures, firstly black stripes were arranged and then the gaps separating the black stripes were filled with respective fluorescent bodies for primary colors to produce a fluorescent film 104 for this example (Fig. 11A). The black stripes were made of a popular material containing graphite as a principal ingredient. The fluorescent bodies were applied to the glass substrate 103 by using a slurry method.

A metal back 105 is normally arranged on the inner surface of the fluorescent film 104. In this

example, a metal back was prepared by producing an Al film by vacuum deposition on the inner surface of the fluorescent film 104 that had been smoothed in a socalled filming process. The face plate 106 may be additionally provided with transparent electrodes (not shown) arranged close to the outer surface of the fluorescent film 104 in order to improve the conductivity of the fluorescent film 104, no such electrodes were used in this example because the metal back proved to be sufficiently conductive.

The fluorescent bodies were carefully aligned with the respective devices before the above described bonding operation.

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The prepared glass container was then evacuated by means of an exhaust pipe (not shown) and an exhaust pump to achieve a sufficient degree of vacuum inside the container. Thereafter, the electroconductive film 2 of each of the devices arranged on the substrate 91 was subjected to an electric forming operation, where a voltage was applied to the device electrodes 5, 6 of the devices by way of the external terminals Doxl through Doxm and Doyl through Doyn to produce an electronemitting region 3 in each electroconductive film 2.

The voltage used in the forming operation had a waveform same as the one shown in Fig. 5B. Referring to Fig. 5B, Tl and T2 were respectively 1 milliseconds and 10 milliseconds and the electric forming operation

was carried out in vacuum of a degree of approximately 1×10^{-6} torr. The wave height (the peak voltage for the forming operation) of the applied pulse voltage was increased stepwise with steps of 0.1 V.

A monitoring device was also prepared without subjecting them to an electric forming operation so that it may be used to monitor the electric resistance of each device during a subsequent chemical reduction process, which will be described hereinafter.

Dispersed fine particles containing palladium oxide as a principal ingredient were observed in the electron-emitting regions 3 of the electron-emitting devices that had been produced in the above process. The fine particles had an average particle diameter of 30 angstroms.

Step i:

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Subsequently, the electroconductive film 4 including an electron-emitting region each of the electron-emitting device was subjected to a chemical reduction process (Fig. 18I).

In this process, the enclosure comprising a face plate 106, a support frame 102 and a rear plate 101 was evacuated by means of an exhaust pump to a degree of vacuum of 1 x 10^{-6} torr and then the devices were heated to 130°C to 200°C for approximately 10 hours in the vacuum. After the chemical reduction process, it was found that the electroconductive film 2 (film of

PdO fine particles) of the control device without an electric forming process had been chemically reduced to become a film of fine particles of Pd metal having an electric resistance per unit area of $5 \times 10^2 \Omega/D$ or a value smaller than the resistance before the chemical reduction by two digits.

Thus, the operation of preparing an electron source was completed as the devices arranged on the substrate 91 had been subjected to an electric forming operation to produce electron-emitting regions 3 and a chemical reduction process.

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Thereafter, the enclosure was evacuated to a degree of vacuum of approximately of 10^{-6} torr and then hermetically sealed by melting and closing the exhaust pipe (not shown) by means of a gas burner.

The apparatus was subjected to a getter process using a high frequency heating technique in order to maintain the degree of vacuum in the apparatus after the sealing operation, where a getter disposed at a predetermined position (not shown) in the enclosure was heated by high frequency heating immediately before the sealing operation to form a film as a result of vapor deposition. The getter is a material containing Ba as a principal component.

25 The electron source having a simple matrix arrangement as described above was then used to produce an image-forming apparatus adapted for the NTSC television

system. The image-forming apparatus was complete with a drive circuit as illustrated in Fig. 12 and described earlier. Pulse modulation was used for the imageforming apparatus.

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The electron-emitting devices of the above image-forming apparatus were then caused to emit electrons by applying a drive voltage thereto through the external terminals Doxl through Doxm and Doyl through Doyn and the emitted electrons were accelerated by applying a high voltage of 10 kV to the metal back 105 via the high voltage terminal Hv so that they collides with the fluorescent film 104 until the latter was energized to emit light and produce images. As the image-forming apparatus of this example had undergone a chemical reduction process for the electroconductive films of the electron-emitting devices in the process of manufacturing them, it has a feature of low energy consumption rate for operation.

(Example 3)

A chemical reduction process was carried out in a reducing atmosphere for this example.

An electron-emitting device having a configuration as illustrated in Figs. 7A, 7B was prepared by following Steps a through e, of which Steps a through d are same as those of Example 1 above. So, only Step e will be described here.

Step e:

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As in the case of Example 1, an electronemitting device comprising a pair of electrodes 5 and
6 and an electroconductive film 4 including an electronemitting region 3 arranged on a substrate 1 (Fig. 3C)
and a monitoring device that had not been subjected to
an electric forming operation (or that had undergone
Steps a through c) were place in a vacuum apparatus as ~
shown in Fig. 4, into which nitrogen gas containing
hydrogen by 2% was introduced from a reducing gas
cylinder as shown in Fig. 19 until it showed a partial
pressure of 1 millitorr at room temperature in the
apparatus, when the devices were heated to temperature
between 130°C and 200°C and kept to that temperature for
approximately an hour.

After the chemical reduction process for an hour, it was found that the electroconductive film containing PdOx as a principal ingredient of the monitoring device without an electric forming process had been chemically reduced to become a film of fine particles of Pd metal having an electric resistance per unit area of 5 x 10^2 Ω/\Box or a value smaller than the resistance before the chemical reduction by two digits.

In an attempt to see the properties of the
electron-emitting device prepared through the preceding
steps, it was observed for electron-emitting performance,
using a gauging system as illustrated in Fig. 4. In

the above observation, the distance H between the anode 34 and the electron-emitting device was 4 mm and the potential of the anode 34 was 1 kV, while the degree of vacuum in the vacuum chamber of the system was held to 1×10^{-6} torr throughout the gauging operation.

A device voltage was applied between the device electrodes 5, 6 of the device to see the device current If and the emission current Ie under that condition. Fig. 6 shows the current-voltage relationships obtained as a result of the observation.

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An emission current Ie began to flow through the device immediately when the device voltage (Vf) became as high as 14 V and a device current Ie of 2.2 milliA and an emission current Ie of 1.1 microA were observed when the device voltage rose to 14 V to provide an electron emission efficiency $\theta = \text{Ie/Ifx100(\$)}$ of 0.05%.

When the device was observed before the chemical reduction process, the film of PdO fine particles (electroconductive film) of the device showed an electric resistance of 3.5 k Ω and the fissured area had an electric resistance of 6.4 k Ω . After the chemical reduction process, it was found that the electric resistance of the film of PdO fine particles of the electron-emitting device that had undergone a chemical reduction process (the device of this example) was as low as 35 Ω , which was negligible when compared

l with that of the fissured area.

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In other words, for an electron-emitting device after a chemical reduction process according to the invention to obtain the same electron emission rate as a 5 device before the process having required a device voltage of 22 V, the device after the process required a power consumption rate of only 31 milliw, whereas it was only 48 milliW for the device before the process, i.e., the former being two thirds of the latter, thus proving a significant saving of power.

Note that the duration of chemical reduction process was as short as an hour and this fact can greatly contribute to raising the rate of manufacturing electron-emitting devices of the type under consideration.

- 15 Additionally, since the chemical reduction process is conducted in an electric furnace under the atmospheric pressure, the entire facility required for manufacturing electron-emitting devices can be remarkably simplified. (Example 4)
- 20 A total of twenty-five electron-emitting devices each having a configuration as shown in Figs. 7A and 7B were prepared.

The process of preparing the electron-emitting devices will be described below in terms of a single device by referring to Figs. 3A to 3C and Figs. 7A and 7B.

1 Step a:

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A silicon oxide film was formed on a thoroughly cleansed soda lime glass plate to a thickness of 0.5 microns by sputtering to produce a substrate 1, on which a pattern of photoresist (RD-2000N-41: available from Hitachi Chemical Co., Ltd.) was formed for a pair of device electrodes and a gap separating the electrodes and then Ti and Ni were sequentially deposited thereon prespectively to thicknesses of 5 nm and 100 nm by vacuum deposition.

The photoresist pattern was dissolved in an organic solvent and the Ni/Ti deposit film was treated by using a lift-off technique to produce a pair of device electrodes 5 and 6 having a width W of 300 microns and separated from each other by a distance L of 20 microns (Fig. 3A).

Step b:

A Cr film was deposited by vacuum deposition on the entire surface of the substrate prepared in Step a and including the device electrodes 5 and 6 to a film thickness of 50 nm and then subjected to a patterning operation, using a mask (not shown) having opening with a length not smaller than L and a width W' for the gap separating the device electrodes and its vicinity. The film was then developed and etched for the opening to expose the gap L separating the electrodes and part of the device electrodes 5, 6, to produce a Cr mask having

- a width W' of 100 μm. Thereafter, organic Pd (ccp4230: available from Okuno Pharmaceutical Co., Ltd.) was applied to the Cr film by means of a spinner, while rotating the film, and baked at 300°C for 10 minutes.
- Thereafter, the Cr film was etched by an acidic etchant and treated by using a lift-off technique to produce an electroconductive film 4 (Fig. 3B).

The produced electroconductive film 4 was made \sim of fine particles containing PdO as a principal ingredient and had a film thickness of 100 angstroms and an electric resistance per unit area of 2 x 10⁴ Ω/\Box .

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Note that the term "a fine particle film" as used herein refers to a thin film constituted of a large number of fine particles that may be loosely

15 dispersed, tightly arranged or mutually and randomly overlapping (to form an island structure under certain conditions). The diameter of fine particles to be used for the purpose of the present invention is that of recognizable fine particles arranged in any of the above described states.

Now, a pair of device electrodes 5, 6 and an electronconductive film 4 were formed on the substrate 1 for all the devices through the above steps.

Step c:

Then, the devices were set in position in a measuring system as illustrated in Fig. 4 and the inside of the vacuum chamber of the system was evacuated

by means of an exhaust pump to a degree of vacuum of 2×10^{-5} torr. Subsequently, a voltage Vf was applied from the power source 31 to the device electrodes 5, 6 of twenty four devices out of the twenty five devices to electrically energize the devices (electric forming process).

Fig. 5B shows the voltage waveform used for the electric forming process.

In Fig. 5B, Tl and T2 respectively denote the

pulse width and the pulse interval of the applied pulse
voltage, which were respectively 1 millisecond and 10
milliseconds for this example. The wave height (the
peak voltage for the forming operation) of the applied
pulse voltage was increased stepwise with steps of 0.1 V.

During the electric forming operation, an additional
pulse voltage of 0.1 V was inserted in each interval of
T2 for measuring the resistance and the application of
pulse voltage was terminated to complete the electric
forming process when the resistance measured by using a

pulsed voltage exceeded about 1 MQ.

In the period from the beginning to the end of an electric forming process, the device current If gets to a maximum level of Imax, the voltage (or the wave height of the pulse voltage) corresponding to Imax being denoted by forming voltage Vform.

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The forming voltage V form for the above devices was approximately 7.0 $\mbox{V.}$

1 Step d:

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Subsequently, a protective film forming operation was conducted on twelve out of the twenty four devices that had been subjected to the electric forming process. In this operation, a pulse voltage as shown in Fig. 5A and having a wave height value of 14 V was applied to the device electrodes 5, 6 of the devices in order to cause them emit electrons. The emitted electrons operated to decompose carbon compounds into carbon atoms, which were deposited on and near the electron-emitting regions 3 of the devices to produce a protective film.

The twelve devices subjected to the protective film forming operation are called devices A, whereas the remaining twelve devices not subjected to the protective film forming operation after the electric forming process are called devices B.

For the protective film forming operation, a pulse voltage was applied to the device electrodes 5, 6 of each device while observing the emission current le in the apparatus of Fig. 4, the inside of which apparatus was maintained to a degree of vacuum of 1.5×10^{-5} torr.

The emission current Ie became saturated in approximately 30 minutes, when the protective film forming operation was terminated.

1 Step e:

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All the devices including the one that had not undergone an electric forming process were then subjected to a chemical reduction process.

In this operation, nitrogen gas containing hydrogen by 2% was introduced through a reducing gas inlet pipe (not shown) under the control of a mass flow controller (not shown) until it showed a partial pressure of 1 millitorr in the vacuum apparatus.

As the twenty five devices were exposed to this atmosphere for an hour, the electroconductive films 4 of the devices containing PdO as a principal ingredient were chemically reduced to become so many films of fine Pd particles that showed an electric resistance per unit area of 5 x 10^2 Ω/D or a value smaller than the resistance before the chemical reduction by two digits.

The change in the electric resistance of the films was confirmed by measuring the electric resistance between the device electrodes (hereinafter referred to as device resistance) of the single electron-emitting device that had not been subjected to an electric forming operation before and after the chemical reduction process. More specifically, the device resistance of the device was 4 k Ω before the chemical reduction and approximately 100 Ω after the chemical reduction.

In numerical terms, when an electron-emitting device prepared in a manner as described above is driven

under the above described condition, a device current of approximately 1 mA flows through the device.

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If the electroconductive film 4 of the device is not chemically reduced, the device voltage shows a drop of approximately 4 V at the electroconductive film 4 due to the relatively high electric resistance of the lateral portions of the film arranged at the opposite ends of the electron emitting region 3 to ineffectively—consume power at a rate of 4 mW.

As seen from the graph of current-voltage relationship of a surface conduction electron-emitting device illustrated in Fig. 6, the emission current sharply or exponentially rises relative to the device voltage when the latter gets to Vth. Therefore, an electroconductive film 4 that has not been treated for chemical reduction not only consumes power ineffectively but also lowers the voltage applied to the electron emitting region 3 and hence the rate of electron emission as the voltage drops at the lateral portions of the film.

So, in order for the emission current of an electron-emitting device that has not been treated for chemical reduction to become equal to that of an electron-emitting device that has undergone a chemical reduction process, the drive voltage of the former device has to be made approximately 4 V higher than that of the latter device.

In other words, a chemical reduction process is highly effective for efficiently driving a surface conduction electron-emitting device with a low voltage and a low energy consumption rate.

In order to further look into the profile and the performance of the surface conduction electron-emitting devices prepared through the above steps, one of the devices A and one of the devices B were picked up and observed through an electron microscope and the remaining devices were tested on a one by one basis in the apparatus of Fig. 4. The electron-emitting device to be tested was separated from the anode 34 by 4 mm and a voltage of 1 kV was applied to the anode 34 while maintaining the inside of the vacuum apparatus to a degree of vacuum of 1 x 10⁻⁶ torr during the test.

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A device voltage of 14 V was applied to each of the tested devices A and B to see the device current If and the emission current Ie.

When the twelve devices A is compared with the twelve devices B, the average device current If of the devices A was 1.0 mA and that of the devices B was 1.2 mA for the device voltage of 14 V whereas the emission current Ie of the former was 0.5 microA and that of the latter was 0.45 microA to provide an electron emission efficiency $\theta = \text{Ie/Ifx100(\$)}$ of 0.05% for the devices A and 0.04% for the devices B. The standard deviation of the dispersed emission current

values relative to the average was approximately 6% for the devices A and approximately 10% for the devices B.

From the above observations, it was proved that the devices A had an ineffective current (part of the device current that does not contribute to electron emission) lower than that of the devices B and the former were also superior to that latter in terms of electron emission efficiency and uniformity.

As a result of electron microscope observation,

it was found that the sampled device A had a protective
film 11 at the interface of the electroconductive film 4
and the substrate 1 near the electron emitting region 3
on both the positive and negative sides as illustrated
in Fig. 20, although the protective film was

particularly remarkable on the positive electrode side.
While a similar film was observed on the sample device
B, it was markedly poor and not found in certain
necessary areas.

When observed through an FE-SEM having a large magnification, it was found that the electroconductive film 4 of fine particles of each of the devices B that had been treated for chemical reduction without a protective film had been partly deformed and displaced in the vicinity of the electron emitting region 3. As the electron emitting region 3 had been partly covered back by the electroconductive film 4, the device electrodes 5 and 6 were slightly short-circuited

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through narrow routes of electric current. This might prove that the electron emitting region 3 had been partly destroyed as a result of chemical reduction.

Contrary to this, such phenomena were not observed on the devices A that had been subjected to chemical reduction with a protective film.

It seemed that the protective film 11 had also been formed in periphery areas of and gaps separating metal fine particles of the electroconductive film 4.
By observing the protective film through a TEM and a Raman spectroscope, it was found that the protective film 11 was composed of carbon mainly in the form of graphite and amorphous carbon or carbon compounds.

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From the above observations, it can safely be concluded that the electron emitting region 3 and the remaining areas of the electroconductive film of fine particles of each of the device B were partly destroyed and displaced during the chemical reduction process as the surface energy was activated on the electroconductive film near and around the electron emitting region 3, leading to differentiated performances among the devices B. On the other hand, the protective film 11 of carbon or carbon compounds formed near and around the electron emitting region 3 of each of the devices A effectively prevented the electron emitting region 3 from being destroyed during the chemical reduction process so that the reduction process proceeded stably

to produce uniform devices A.

(Example 5)

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This example relates to an image-forming apparatus comprising a plurality of electron-emitting devices of the type A produced by the method of Example 2, where the electroconductive films 4 are made of SnO₂ and the electron-emitting devices are arranged to form a simple matrix.

Fig. 15 shows a schematic partial plan view of

the electron source and Fig. 16 shows a schematic

partial sectional view taken along line A-A' of Fig.

15, while Figs. 17A - 17F and 18G - 18I illustrate

schematic partial sectional views of the electron

source shown in different manufacturing steps. Note

that same or similar components are respectively

designated by same reference symbols throughout

Figs. 15 through 18I.

91 denotes a substrate and 92 and 93 respectively denote X- and Y-directional wirings (which may be called lower and upper wirings respectively) that correspond to Dxm and Dyn in Fig. 9. Otherwise, the electron source comprises electron-emitting devices, each having an electroconductive film 4 and a pair of device electrodes 5 and 6, an interlayer insulation layer 161 and a number of contact holes, each of which is used to connect a device electrode 5 with a related lower wiring 92.

Now, the steps of manufacturing an electron

source and an image-forming apparatus incorporating such as electron source used in this example will be described in detail.

Step a:

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After thoroughly cleansing a soda lime glass plate a silicon oxide film was formed thereon to a thickness of 0.5 micrometers by sputtering to produce a substrate 91, on which Cr and Au were sequentially laid to thicknesses of 5.0 nm and 600 nm respectively and then a photoresist (AZ1370: available from Hoechst Corporation) was formed thereon by means of a spinner, while rotating the film, and baked. Thereafter, a photo-mask image was exposed to light and developed to produce a resist pattern for the lower wirings 92 and then the deposited Au/Cr film was wet-etched to produce lower wiring 82 having a desired profile (Fig. 17A). Step b:

A silicon oxide film was formed as an interlayer insulation layer 161 to a thickness of 1.0 micrometer by RF sputtering (Fig. 17B). Step c:

A photoresist pattern was prepared for producing contact holes 162 in the silicon oxide film deposited in Step b, which contact holes 162 were then actually formed by etching the interlayer insulation layer 161, using the photoresist pattern for a mask (Fig. 17C). RIE (Reactive Ion Etching) using CF_4 and H_2 gas was

employed for the etching operation.

Step d:

Thereafter, a pattern of photoresist (RD-2000N-41: available from Hitachi Chemical Co., Ltd.) was formed for

- pairs of device electrodes 5 and 6 and gaps Ll separating the respective pairs of electrodes and then Ti and Ni were sequentially deposited thereon respectively to thicknesses of 5.0 nm and 100 nm by vacuum deposition. The photoresist pattern was
- dissolved by an organic solvent and the Ni/Ti deposit
 film was treated by using a lift-off technique to produce
 pairs of device electrodes 5 and 6, each pair having a
 width of 300 micrometers and separated from each other
 by a distance L1 of 20 micrometers (Fig. 17D).
- 15 Step e:

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After forming a photoresist pattern on the device electrodes 5, 6 for upper wirings 93, Ti and Au were sequentially deposited by vacuum deposition to respective thicknesses of 5.0 nm and 500 nm and then unnecessary areas were removed by means of a lift-off technique to produce upper wirings 93 having a desired profile (Fig. 17E).

Step f:

Electroconductive films 2 made of a mixture of

Sn and SnO₂ were produced by sputtering Sn in an oxygen atmosphere, using a metal mask that had an opening for the gap Ll separating the device electrodes and its

- vicinity of each device (Fig. 17F). The width of the electroconductive film 2 was 100 micrometers for this example. The formed electroconductive films 2 were made of fine particles containing SnO₂ as a principal
- ingredient and had a film thickness of 70 angstroms and an electric resistance per unit area of 2.5 x 10⁴ Ω/□. Note that the term "a fine particle film" as used herein refers to a thin film constituted of a large number of fine particles that may be loosely dispersed,
- tightly arranged or mutually and randomly overlapping
 (to form an island structure under certain conditions).

 The diameter of fine particles to be used for the purpose of the present invention is that of recognizable fine particles arranged in any of the above described

15 states.

Step g:

The Cr film 171 and the baked electroconductive film 2 were etched by using an acidic etchant to produce a desired pattern (Fig. 18G).

20 Step h:

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Then, a pattern for applying photoresist to the entire surface area except the contact holes 162 was prepared and Ti and Au were sequentially deposited by vacuum deposition to respective thicknesses of 5.0 nm and 500 nm. Any unnecessary areas were removed by means of a lift-off technique to consequently bury the contact holes 162 (Fig. 18H).

Now, lower wirings 92, an interlayer insulation layer 161, upper wirings 93, and devices comprising pairs of device electrodes 5 and 6 and electroconductive films 2 were produced on the substrate 91.

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Then, an electron source comprising the above electron source substrate and an image-forming apparatus incorporating such an electron source were prepared.

This will be described below by referring to Figs. 10, 11A and 11B.

The substrate 91 carrying thereon a large number of devices prepared in a manner as described above was rigidly fitted to a rear plate 101 and thereafter a face plate 106 (prepared by forming a fluorescent film 104 and a metal back 105 on a glass substrate 103) was arranged 5 mm above the substrate 91 by interposing a support frame 102 therebetween. Frit glass was applied to junction areas of the face plate 106, the support frame 102 and the rear plate 101, which were then baked at 400°C for 10 minutes or more in the atmosphere and bonded together to a hermetically sealed condition (Fig. 10).

The substrate 91 was also firmly bonded to the rear plate 101 by means of frit glass.

In Fig. 10, reference numerals 92 and 93
25 respectively denote X- and Y-directional wirings.

While the fluorescent film 104 may be solely made of fluorescent bodies if the image-forming apparatus

is for black and white pictures, firstly black stripes
were arranged and then the gaps separating the black
stripes were filled with respective fluorescent bodies
for primary colors to produce a fluorescent film 104
for this example (Fig. 11A).

The black stripes were made of a popular material containing graphite as a principal ingredient.

The fluorescent bodies were applied to the glass substrate 103 by using a slurry method. A metal back

10 105 is normally arranged on the inner surface of the fluorescent film 104. In this example, a metal back was prepared by producing an Al film by vacuum deposition on the inner surface of the fluorescent film 104 that had been smoothed in a so-called electric

15 filming process.

The face plate 106 may be additionally provided with transparent electrodes (not shown) arranged close to the outer surface of the fluorescent film 104 in order to improve the conductivity of the fluorescent film 104, no such electrodes were used in this example because the metal back proved to be sufficiently conductive.

The fluorescent bodies were carefully aligned with the respective devices before the above described bonding operation.

The prepared glass container was then evacuated by means of an exhaust pipe (not shown) and an exhaust

- pump to achieve a sufficient degree of vacuum inside
 the container. Thereafter, the electroconductive
 film 2 of each of the devices arranged on the substrate
 91 was subjected to an electric forming operation,
- where a voltage was applied to the device electrodes 5, 6 of the devices by way of the external terminals Doxl through Doxm and Doyl through Doyn to produce an electron-emitting region 3 in each electroconductive film 2.
- The voltage used in the forming operation had a waveform same as the one shown in Fig. 5B.

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Referring to Fig. 5B, Tl and T2 were respectively 1 milliseconds and 10 milliseconds and the electric forming operation was carried out in vacuum of a degree of approximately 1 x 10^{-6} torr. The wave height (the peak voltage for the forming operation) of the applied pulse voltage was increased stepwise with steps of 0.1 V. During the electric forming operation, an additional pulse voltage of 0.1 V was inserted in each interval of T2 for measuring the resistance and the application of pulse voltages was terminated to complete the electric forming process when the resistance measured by using a pulsed voltage exceeded about 1 M Ω .

The forming voltage Vform for the above devices was approximately $4.0\ V.$

Fine particles containing SnOx as a principal

ingredient and having an average diameter of 4.0 nm were observed to be dispersed throughout the electron emitting regions 3 of the electron-emitting devices procuded in a manner as described above.

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Subsequently, a protective film forming operation was conducted on each of the devices under a vacuum condition same as that of the electric forming process, where a pulse voltage as shown in Fig. 5A was applied to the device electrodes 5 and 6 of the electron-emitting devices 94 through the external electrodes Doxl through Doxm and Doyl through Doyn.

In this operation, a pulse voltage having a wave height value of 14 V was applied to the device electrodes 5, 6 of the devices in order to cause them emit electrons, while observing the emission current Ie. The emission current Ie became saturated in approximately 30 minutes, when the protective film forming operation was terminated.

All the devices were then subjected to a chemical reduction process.

In this operation, nitrogen gas containing hydrogen by 2% was introduced through a reducing gas inlet pipe (not shown) under the control of a mass flow controller (not shown) until it showed a partial pressure of 1 millitorr in the vacuum apparatus.

As the devices were exposed to this atmosphere for an hour, the electroconductive films 4 of the devices

containing SnO_2 as a principal ingredient were chemically reduced to become so many films of fine Sn particles that showed an electric resistance per unit area of 6 x 10^2 Ω/\Box or a value smaller than the resistance before the chemical reduction by two digits.

Thus, the operation of preparing electronemitting devices 94 were completed as they had been subjected to an electric forming operation, a protective film forming operation and a chemical reduction process to produce electron emitting regions 3.

Thereafter, the enclosure was evacuated to a degree of vacuum of approximately 10^{-6} torr and then hermetically sealed by melting and closing the exhaust pipe (not shown) by means of a gas burner.

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The apparatus was subjected to a getter process using a high frequency heating technique in order to maintain the degree of vacuum in the apparatus after the sealing operation, where an getter disposed at a predetermined position (not shown) in the enclosure was heated by high frequency heating immediately before the sealing operation to form a film as a result of vapor deposition. The getter is a material containing Ba as a principal component.

The electron-emitting devices of the above
image-forming apparatus were then caused to emit
electrons by applying scanning signals and modulation
signals generated by a signal generating means (not

through Doxm and Doyl through Doyn and the emitted electrons were accelerated by applying a high voltage of greater than several kV to the metal back 105 or a transparent electrode (not shown) via the high voltage terminal HV so that they collides with the fluorescent film 104 until the latter was energized to emit light and produce images.

The electron source prepared for this example

consumed little power with a reduced drive voltage so
that the load applied to the circuits that are
peripheral to the electron source was also reduced.

Consequently the image-forming apparatus incorporating
such an electron source was prepared at low cost.

The image-forming apparatus operated stably with a reduced power consumption rate to display excellent images.

(Example 6)

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This example deals with an image-forming

apparatus comprising a large number of surface conduction electron-emitting devices and control electrodes (grids).

Since an apparatus to be dealt in this example can be prepared in a way as described above concerning the image-forming apparatus of Example 5, the method of manufacturing the same will not be described any further.

Each of the surface conduction electron-emitting

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- devices of the device electrode had a gap of 50 micrometers between the device electrodes. A chemical reduction process was conducted on the devices in a manner similar to the one described earlier for
- Example 5. In this reduction process, the devices were exposed to nitrogen gas containing hydrogen by 2% and having a partial pressure of 100 mtorr for 30 minutes.

The configuration of the apparatus will be

10 described in terms of the electron source of the
apparatus prepared by arranging a number of surface
conduction electron-emitting devices.

Fig. 13B shows a schematic plan view the electron source which is a ladder type. Referring to

15 Fig. 13B, 144 denotes an electron source substrate typically made of soda lime glass and 131 denotes an surface conduction electron-emitting device arranged on the substrate 144 and shown in a dotted circle.

Whereas Dx'l through Dx'6 that are commonly indicated by 132 denote common wirings for the surface conduction electron-emitting devices.

The surface conduction electron-emitting devices 131 were arranged in rows running along X-direction (hereinafter referred to as device rows) and the surface conduction electron-emitting devices of each row are connected in parallel by a pair of common wirings running along the rows. Note that a single

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common wiring is arranged between any two adjacent device rows to serve for the both rows as a wiring electrode. For instance, common wiring or wiring electrode Dx'2 serves for both the first device row and the second device row.

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This arrangement of wiring electrodes is advantageous in that, if compared with the arrangement of Fig. 13A, the space separating any two adjacent rows of surface conduction electron-emitting devices can be significantly reduced in Y-direction.

In the apparatus of this example comprising the above described electron source, the electron source can drive any device rows independently by applying an appropriate drive voltage to the related wiring electrodes. More specifically, a voltage exceeding the threshold voltage level for electron emission is applied to the device rows to be driven to emit electrons, whereas a voltage not exceeding the threshold voltage level for electron emission (e.g., 0 V) is applied to the remaining device rows. (A voltage exceeding the threshold voltage level and used for the purpose of the invention is expressed by drive voltage Vope[V] hereinafter.)

For instance, only the devices of the third row
can be driven to operate by applying O[V] to the wiring
electrodes Dx'l through Dx'3 and Vope[V] to the wiring
electrodes Dx'4 through Dx'6. Consequently,

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Vope-0 = Vope[V] is applied to the devices of the third row, whereas O[V], 0-0 = O[V] or Vope-Vope = O[V], is applied to all the devices of the remaining rows.

Likewise, the devices of the second and the fifth rows can be driven to operate simultaneously by applying O[V] to the wiring electrodes Dx'1, Dx'2 and Dx'6 and Vope[V] to the wiring electrodes Dx'3, Dx'4 and Dx'5. In this way, the devices of any device row of this electron source can be driven selectively.

While each device row has twelve (12) surface conduction electron-emitting devices arranged along the X-direction in the electron sources of Fig. 13B, the number of devices to be arranged in a device row is not limited thereto and a greater number of devices may alternatively be arranged. Additionally, while there are five (5) device rows in the electron source, the number of device rows is not limited thereto and a greater number of device rows may alternatively be arranged.

Now, a panel type CRT incorporating an electron source of the above described type will be described.

Fig. 14 is a schematic perspective view of a panel type CRT incorporating an electron source as illustrated in Fig. 13B. In Fig. 14, VC denote a glass vacuum container provided with a face plate for displaying images as a component thereof. A transparent electrode made of ITO is arranged on the inner surface of

the face plate and red, green and blue fluorescent members are applied onto the transparent electrode in the form of a mosaic or stripes without interfering with each other. To simplify the illustration, the transparent electrodes and the fluorescent members are collectively indicated by reference symbol 104 in Fig. 14. Black stripes known in the field of CRT may be arranged to fill the blank areas of the transparent electrode that are not occupied by the fluorescent stripes. Similarly, a metal back layer of any known 10 type may be arranged on the fluorescent members. The transparent electrode is electrically connected to the outside of the vacuum container by way of a terminal Hv so that an voltage may be applied thereto in order to accelerate electron beams. 15

In Fig. 14, 144 denotes the substrate of the electron source rigidly fitted to the bottom of the vacuum container VC, on which a number of surface conduction electron-emitting devices are arranged in a manner as described above by referring to Fig. 13B. The wiring electrodes of the device rows are electrically connected to respective electrode terminals Dox1 through Dox(m+1) arranged on a lateral panel of the apparatus so that electric drive signals may be applied thereto from outside of the vacuum enclosure (m = 200 for the apparatus of this example).

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Stripe-shaped grid electrodes 140 are arranged

in the middle between the substrate 144 and the face plate 106. There are provided a total of 200 grid electrodes GR arranged in a direction perpendicular to that of the device rows (or in the Y-direction) and each grid electrode has a given number of openings 141 for allowing electron beams to pass therethrough. More specifically, a circular opening 141 is provided for each surface conduction electron-emitting device. The grid electrodes are electrically connected to the outside of the vacuum container via respective electric terminals G1 through Gn (n = 200 for the apparatus of this example).

The above described display panel comprises surface conduction electron-emitting devices arranged in 200 device rows and 200 grid electrodes to form an X-Y matrix of 200 x 200. With such an arrangement, an image can be displayed on the screen on a line by line basis by applying a modulation signal to the grid electrodes for a single line of an image in synchronism with the operation of driving (scanning) the surface conduction electron-emitting devices on a row by row basis to control the irradiation of electron beams onto the fluorescent film.

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Fig. 22 is a block diagram of an electric

25 circuit to be used for driving the display panel of the above described electron source having a ladder-like arrangement in order to display images according to TV

signals of the NTSC system. Pulse modulation was used for the image-forming apparatus.

The electron-emitting devices of the above image-forming apparatus were then caused to emit electrons by applying scanning signals and modulation signals generated by a signal generating means thereto through the external terminals Doxl through Dox(m+1) and Doyl through Doyn and the emitted electrons were accelerated by applying a high voltage of 10 kV to a metal back (not shown) or a transparent electrode (not shown) via the high voltage terminal HV so that they collides with the fluorescent film 104 until the latter was energized to emit light and produce images.

The electron source prepared for this example consumed little power with a reduced drive voltage so that the load applied to the circuits that are peripheral to the electron source was also reduced. Consequently the image-forming apparatus incorporating such an electron source was prepared at low cost.

20 (Example 7)

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Contrary to Example 1 where the film of fine PdO particles of an electron-emitting device was chemically reduced by heating in vacuum, the film of fine particles of the electron-emitting device of this example was heated and reduced in a reducing solution.

The electron-emitting device having a configuration as illustrated in Figs. 7A and 7B was

prepared by following Steps a through e, of which
Steps a through d are same as those of Example 1
above. So, only Step e will be described here.

• 6.

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As in the case of Example 1, the device

comprising a pair of device electrodes 5, 6 and an
electroconductive film 4 including an electron emitting
region 3 arranged on a substrate 1 was subjected to a
chemical reduction process as described below.

- As shown in Fig. 21, the electron-emitting device was placed in a liquid of 100% formic acid (reducing liquid) and heated to temperature between 50°C and 60°C for two minutes by means of a heater which is connected to a temperature controller.
- Consequently, the PdO in the form of a film of fine particles of the device that has not undergone an electric forming process was chemically reduced to become metal Pd also in the form a film of fine particles having an electric resistance per unit area of $5 \times 10^2 \,\Omega/\Box$ or a value smaller than the resistance before the chemical reduction by two digits.

In an attempt to see the properties of the flat type electron-emitting device prepared through the preceding steps, it was observed for electron-emitting performance, using a measuring system as illustrated in Fig. 4. In the above observation, the distance H between the anode 34 and the electron-emitting device was 4 mm

and the potential of the anode 34 was 1 kV, while the degree of vacuum in the vacuum chamber of the system was held to 1 x 10^{-6} torr throughout the gauging operation.

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A device voltage was applied between the device electrodes 5, 6 of the device to see the device current If and the emission current Ie under that condition.

Fig. 6 shows the current-voltage relationships obtained as a result of the observation.

The emission current Ie of the device began to increase sharply when the device voltage (Vf) became as high as 8 and a device current If of 2.0 milliA and an emission current Ie of 1.2 microA were observed when the device voltage rose to 14 V to provide an electron emission efficiency $\theta = Ie/Ifx100(\$)$ of 0.06%.

When the device was observed before the chemical reduction process, the film of PdO fine particles (electroconductive film) of the device showed an electric resistance of 3.5 k Ω and the fissured area had an electric resistance of 7 k Ω .

After the chemical reduction process, it was found that the electric resistance of the film of PdO fine particles of the electron-emitting device that had undergone an chemical reduction process (the device of this example) was as low as 30 Ω , which was negligible when compared with that of the fissured area.

In other words, for an electron-emitting device

after a chemical reduction process according to the invention to obtain the same electron emission rate as a device before the process having required a device voltage of 21 V, the device after the process required a power consumption rate of only 28 milliw, whereas it was 42 milliw for the device before the process, i.e., the former being two thirds of the latter, thus proving a significant saving of power.

Process was as short as two hour or much shorter than that of the device of Example 1, which was ten hours and this fact can further contribute to raising the rate of manufacturing electron-emitting devices of the type under consideration. Additionally, since the chemical reduction process does not require any gas nor vacuum apparatus, the entire facility required for manufacturing electron-emitting devices can be remarkably simplified.

20 Fig. 23 is a block diagram of the display apparatus comprising an electron source realized by arranging a number of surface conduction electron-emitting devices and a display panel and designed to display a variety of visual data as well as pictures of television transmission in accordance with input signals coming from different signal sources.

(Example 8)

Referring to Fig. 23, the apparatus comprises

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a display panel 500, a display panel drive circuit 501, 1 a display panel controller 502, a multiplexer 503, a decoder 504, an input/output interface circuit 505, a CPU 506, an image generation circuit 507, image memory interface circuits 508, 509 and 510, an image input interface circuit 511, TV signal receiving circuits 512 and 513 and an input section 514. If the display apparatus is used for receiving television signals that are constituted by video and audio signals, circuits, speakers and other devices are required for receiving, 10 separating, reproducing, processing and storing audio signals along with the circuits shown in the drawing. However, such circuits and devices are omitted here in view of the scope of the present invention.

Now, the components of the apparatus will be described, following the flow of image data therethrough.

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Firstly, the TV signal reception circuit 513 is a circuit for receiving TV image signals transmitted via a wireless transmission system using electromagnetic waves and/or spatial optical telecommunication networks.

The TV signal system to be used is not limited to a particular one and any system such as NTSC, PAL or SECAM may feasibly be used with it. It is particularly suited for TV signals involving a larger number of scanning lines (typically of a high definition TV system such as the MUSE system) because it can be used for a large display panel comprising a large number of

1 pixels.

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The TV signals received by the TV signal reception circuit 513 are forwarded to the decoder 504.

Secondly, the TV signal reception circuit 512 is a circuit for receiving TV image signals transmitted via a wired transmission system using coaxial cables and/or optical fibers. Like the TV signal reception circuit 513, the TV signal system to be used is not limited to a particular one and the TV signals received by the circuit are forwarded to the decoder 504.

The image input interface circuit 511 is a circuit for receiving image signals forwarded from an image input device such as a TV camera or an image pick-up scanner. It also forwards the received image signals to the decoder 504.

The image memory interface circuit 510 is a circuit for retrieving image signals stored in a video tape recorder (hereinafter referred to as VTR) and the retrieved image signals are also forwarded to the decoder 504.

The image memory interface circuit 509 is a circuit for retrieving image signals stored in a video disc and the retrieved image signals are also forwarded to the decoder 504.

The image memory interface circuit 508 is a circuit for retrieving image signals stored in a device for storing still image data such as so-called still

disc and the retrieved image signals are also forwarded to the decoder 504.

The input/output interface circuit 505 is a circuit for connecting the display apparatus and an external output signal source such as a computer, a computer network or a printer. It carries out input/output operations for image data and data on characters and graphics and, if appropriate, for control signals and numerical data between the CPU 506 of the display apparatus and an external output signal source.

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The image generation circuit 507 is a circuit for generating image data to be displayed on the display screen on the basis of the image data and the data on characters and graphics input from an external output signal source via the input/output interface circuit 505 or those coming from the CPU 506. The circuit comprises reloadable memories for storing image data and data on characters and graphics, read-only memories for storing image patterns corresponding given character codes, a processor for processing image data and other circuit components necessary for the generation of screen images.

Image data generated by the circuit for display are sent to the decoder 504 and, if appropriate, they

25 may also be sent to an external circuit such as a computer network or a printer via the input/output interface circuit 505.

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The CPU 506 controls the display apparatus and carries out the operation of generating, selecting and editing images to be displayed on the display screen.

For example, the CPU 506 sends control signals to the multiplexer 503 and appropriately selects or combines signals for images to be displayed on the display screen.

At the same time it generates control signals for the display panel controller 502 and controls the operation of the display apparatus in terms of image display frequency, scanning method (e.g., interlaced scanning or non-interlaced scanning), the number of scanning lines per frame and so on.

The CPU 506 also sends out image data and data on characters and graphic directly to the image generation circuit 507 and accesses external computers and memories via the input/output interface circuit 505 to obtain external image data and data on characters and graphics.

The CPU 506 may additionally be so designed as to participate other operations of the display apparatus including the operation of generating and processing data like the CPU of a personal computer or a word processor. The CPU 506 may also be connected to an external computer network via the input/output interface circuit 505 to carry out numerical computations and other operations, cooperating therewith.

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The input section 514 is used for forwarding the instructions, programs and data given to it by the operator to the CPU 506. As a matter of fact, it may be selected from a variety of input devices such as

keyboards, mice, joy sticks, bar code readers and voice recognition devices as well as any combinations thereof.

The decoder 504 is a circuit for converting various image signals input via said circuits 507 through 513 back into signals for three primary colors, luminance signals and I and Q signals. Preferably, the decoder 504 comprises image memories as indicated by a dotted line in Fig. 23 for dealing with television signals such as those of the MUSE system that require image memories for signal conversion.

15 The provision of image memories additionally facilitates the display of still images as well as such operations as thinning out, interpolating, enlarging, reducing, synthesizing and editing frames to be optionally carried out by the decoder 504 in
20 cooperation with the image generation circuit 507 and the CPU 506.

The multiplexer 503 is used to appropriately select images to be displayed on the display screen according to control signals given by the CPU 506.

In other words, the multiplexer 503 selects certain converted image signals coming from the decoder 504 and sends them to the drive circuit 501. It can also

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divide the display screen in a plurality of frames to display different images simultaneously by switching from a set of image signals to a different set of image signals within the time period for displaying a single frame.

The display panel controller 502 is a circuit for controlling the operation of the drive circuit 501 according to control signals transmitted from the CPU ~ 506. Among others, it operates to transmit signals to the drive circuit 501 for controlling the sequence of operations of the power source (not shown) for driving the display panel in order to define the basis operation of the display panel.

It also transmits signals to the drive circuit 501 for controlling the image display frequency and the scanning method (e.g., interlaced scanning or non-interlaced scanning) in order to define the mode of driving the display panel.

If appropriate, it also transmits signals to the
drive circuit 501 for controlling the quality of the
images to be displayed on the display screen in terms
of luminance, contrast, color tone and sharpness.

The drive circuit 50l is a circuit for generating drive signals to be applied to the display panel 500.

25 It operates according to image signals coming from said multiplexer 503 and control signals coming from the display panel controller 502.

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A display apparatus according to the invention and having a configuration as described above and illustrated in Fig. 23 can display on the display panel 500 various images given from a variety of image data sources.

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More specifically, image signals such as television image signals are converted back by the decoder 504 and then selected by the multiplexer 503 before sent to the drive circuit 501. On the other hand, the display controller 502 generates control signals for controlling the operation of the drive circuit 501 according to the image signals for the images to be displayed on the display panel 500.

The drive circuit 501 then applies drive signals to the display panel 500 according to the image signals and the control signals. Thus, images are displayed on the display panel 500.

All the above described operations are controlled by the CPU 506 in a coordinated manner.

The above described display apparatus can not only select and display particular images out of a number of images given to it but also carry out various image processing operations including those for enlarging, reducing, rotating, emphasizing edges of, thinning out, interpolating, changing colors of and modifying the aspect ratio of images and editing operations including those for synthesizing, erasing,

1 connecting, replacing and inserting images as the image memories incorporated in the decoder 504, the image generation circuit 507 and the CPU 506 participate such operations.

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Although not described with respect to the above embodiment, it is possible to provide it with additional circuits exclusively dedicated to audio signal processing and editing operations.

Thus, a display apparatus according to the

invention and having a configuration as described above
can have a wide variety of industrial and commercial
applications because it can operate as a display
apparatus for television broadcasting, as a terminal
apparatus for video teleconferencing, as an editing

apparatus for still and movie pictures, as a terminal
apparatus for a computer system, as an OA apparatus such
as a word processor, as a game machine and in many other
ways.

an example of possible configuration of a display apparatus comprising a display panel provided with an electron source prepared by arranging a number of surface conduction electron-emitting devices and the present invention is not limited thereto. For example, some of the circuit components of Fig. 23 may be omitted or additional components may be arranged there depending on the application.

1 For instance, if a display apparatus according to the invention is used for visual telephone, it may be appropriately made to comprise additional components such as a television camera, a microphone, lighting equipment and transmission/reception circuits including a modem.

Since a display apparatus according to the invention comprises a display panel that is provided with an electron source prepared by arranging a large number of surface conduction electron-emitting device and hence adaptable to reduction in the depth, the overall apparatus can be made very thin.

Additionally, since a display panel comprising an electron source prepared by arranging a large number of surface conduction electron-emitting devices is adapted to have a large display screen with an enhanced luminance and provide a wide angle for viewing, it can offer really impressive scenes to the viewers with a sense of presence.

20 [Advantages of the Invention]

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As described in detail above, the present invention make it possible to reduce the drive voltage and the power consumption rate of an electron-emitting device and hence provide an energy saving electron source and a high quality image-forming apparatus incorporating such an electron source.

Additionally, according to the invention, since

it is now possible to provide a large gap between the device electrodes of an electron-emitting device without significantly consuming power, electron-emitting devices can be manufactured on a mass

5 production basis without particularly paying attention to the precision of printing operations.

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1 WHAT IS CLAIMED IS:

1. A method of manufacturing an electronemitting device comprising a pair of oppositely disposed electrodes and an electroconductive film inclusive of an electron-emitting region arranged between said electrodes characterized in that said method comprises a processing step of reducing the electric resistance of the electroconductive film arranged between the electrodes.

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- 2. A method of manufacturing an electronemitting device according to claim 1, wherein said electroconductive film arranged between said electrodes mainly contains one or more oxides before the reducing step and one or more metals after the reducing step.
- 3. A method of manufacturing an electron-emitting device according to claim 1, wherein said electroconductive film is made of at least an oxide selected from PdO, SnO₂, In₂O₃, PbO, MoO and MoO₂ or a mixture of a metal selected from Pd, Ru, Ag, Ti, In, Cu, Cr, Fe, Zn, Sn, W and Pb and said oxide or oxides.
- 4. A method of manufacturing an electron25 emitting device according to claim 1, wherein said
 processing step of reducing the electric resistance of
 the electroconductive film arranged between the electrodes

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- 1 is a step of chemically reducing the electroconductive film.
- 5. A method of manufacturing an electron5 emitting device according to claim 4, wherein said chemical reduction step includes a step of heating said electroconductive film in vacuum.
- 6. A method of manufacturing an electron10 emitting device according to claim 4, wherein said chemical reduction step includes a step of heating said electroconductive film in an atmosphere of reducing gas.
- 7. A method of manufacturing an electron-15 emitting device according to claim 6, wherein said reducing gas contains hydrogen.
- 8. A method of manufacturing an electron-emitting device according to claim 4, wherein said20 chemical reduction step includes a step of dipping said electroconductive film in a reducing solution.
- 9. A method of manufacturing an electron-emitting device according to claim 8, wherein said25 reducing solution contains formic acid.
 - 10. A method of manufacturing an electron-

- emitting device according to one of claims 1 through 9,
 wherein said processing step of reducing the electric
 resistance of said electroconductive film arranged
 between said electrodes is conducted after a step of
 producing a high resistance area in said electroconductive
 film arranged between said electrodes.
- emitting device according to claim 10, wherein said step
 of producing a high resistance area in said
 electroconductive film includes a step of electrically
 forming said electroconductive film arranged between
 said electrodes.
- 12. A method of manufacturing an electronemitting device according to one of claims 1 through
 9, wherein it further comprises a step of depositing
 carbon or a carbon compounds on said electroconductive
 film.

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13. A method of manufacturing an electronemitting device according to claim 12, wherein said step
of reducing the electric resistance of said
electroconductive film arranged between said electrodes
is conducted after said step of depositing carbon or a
carbon compounds on said electroconductive film.

- 14. A method of manufacturing an electronemitting device according to claim 12, wherein said
 step of depositing carbon or a carbon compounds on
 said electroconductive film includes a step of applying
 in an atmosphere of the carbon compounds a voltage to
 said electroconductive film arranged between said
 electrodes.
- emitting device for emitting electrons in accordance with input signals characterized in that said electronemitting device is produced by a manufacturing method according to one of claims 1 through 9.
- 16. An electron source comprising a plurality of rows of electron-emitting devices having respective pairs of terminals connected to common wirings and a modulation means for modulating electron beams emitted from said electron-emitting devices in accordance with input signals characterized in that said electron-emitting devices are produced by a manufacturing method according to one of claims 1 through 9.
- 17. An electron source comprising a plurality of electron-emitting devices for emitting electron beams in accordance with input signals, said electron-emitting devices being connected respectively to m X-directional

- wirings and n Y-directional wirings, said wiring being electrically insulated from one another, characterized in that said electron-emitting devices are produced by a manufacturing method according to one of claims 1 through 9.
- 18. An image-forming apparatus comprising an electron source and an image-forming member for forming images in accordance with input signals characterized

 10 in that said electron source is an electron source according to claim 15.
- 19. An image-forming apparatus according to claim 18, wherein said image-forming member comprises a fluorescent body.
- 20. An image-forming apparatus comprising an electron source and an image-forming member for forming images in accordance with input signals characterized in that said electron source is an electron source according to claim 16.
- 21. An image-forming apparatus according to claim 20, wherein said image-forming member comprises a fluorescent body.
 - 22. An image-forming apparatus comprising

an electron source and an image-forming member for forming images in accordance with input signals characterized in that said electron source is an electron source according to claim 17.

23. An image-forming apparatus according to claim 22, wherein said image-forming member comprises a fluorescent body.

ABSTRACT OF THE DISCLOSURE

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An electron-emitting device comprises a pair of oppositely disposed electrodes and an electroconductive film inclusive of an electron-emitting region arranged between the electrodes. The electric resistance of the electroconductive film is reduced after forming the electron-emitting region in the course of manufacturing the electron-emitting device.

FIG. 1A

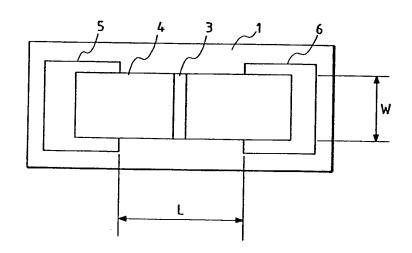
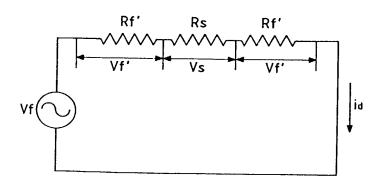
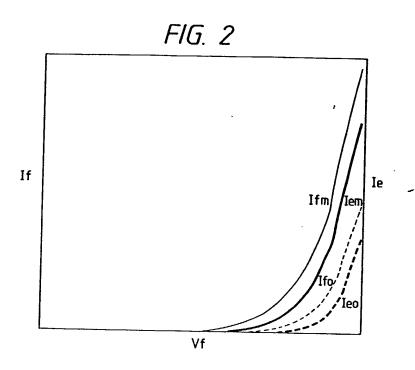
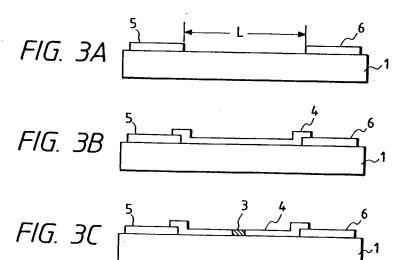


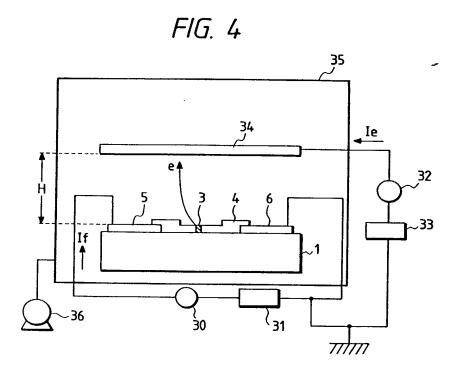
FIG. 1B

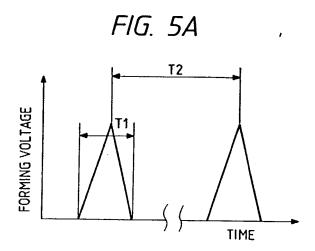


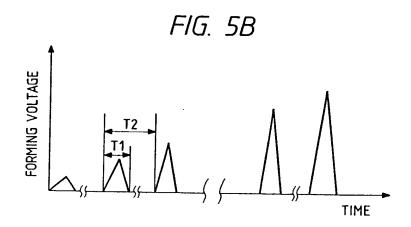
1

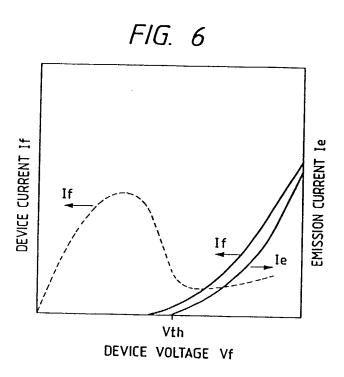


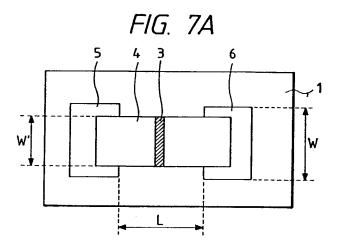


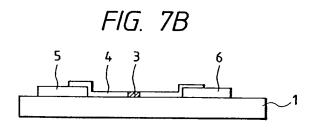












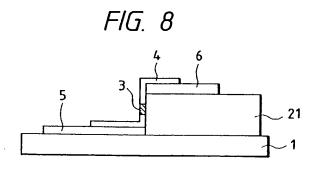
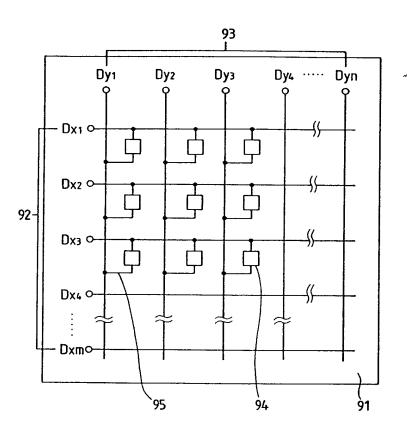
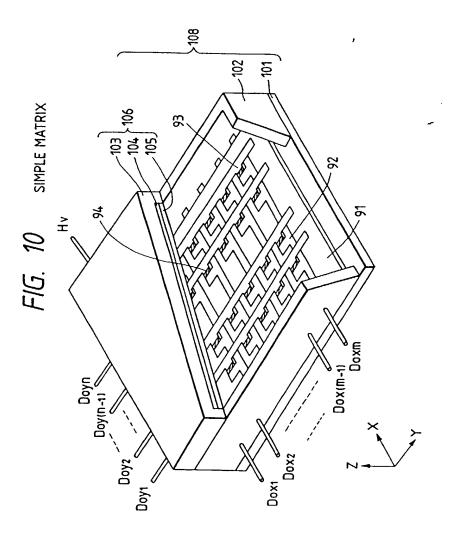
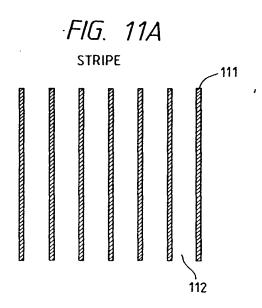


FIG. 9







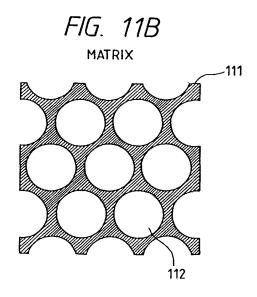
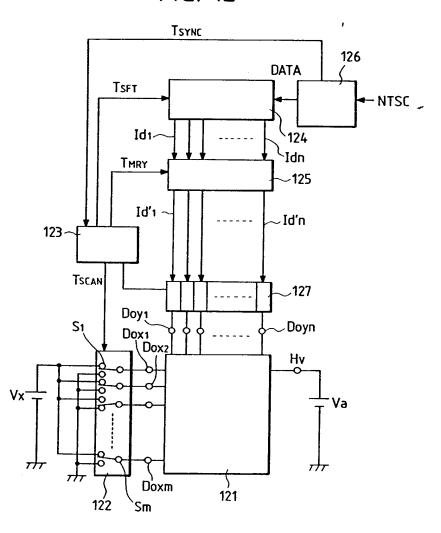
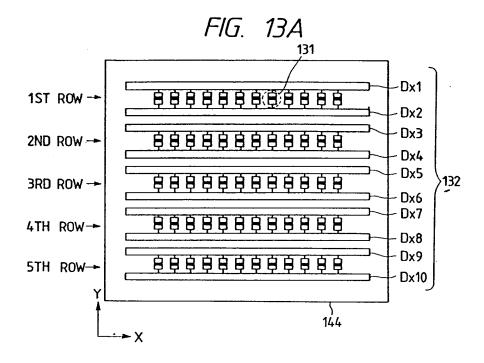
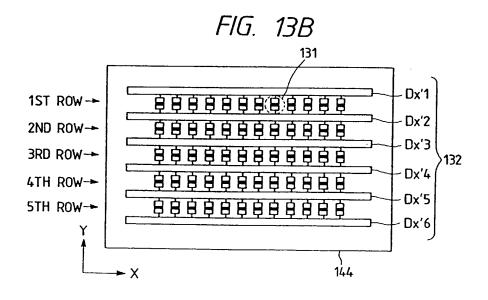
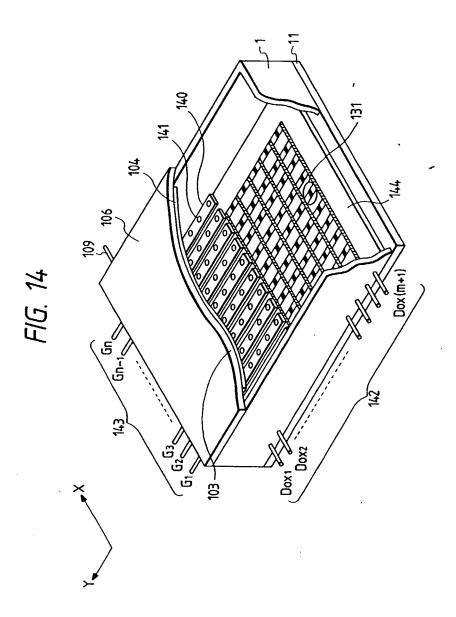


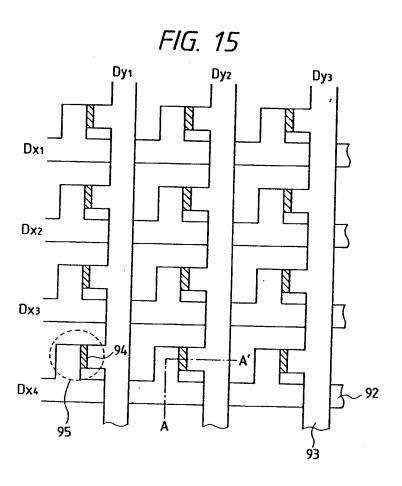
FIG. 12

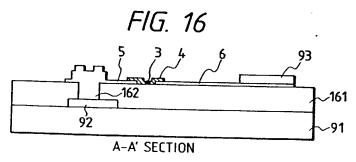




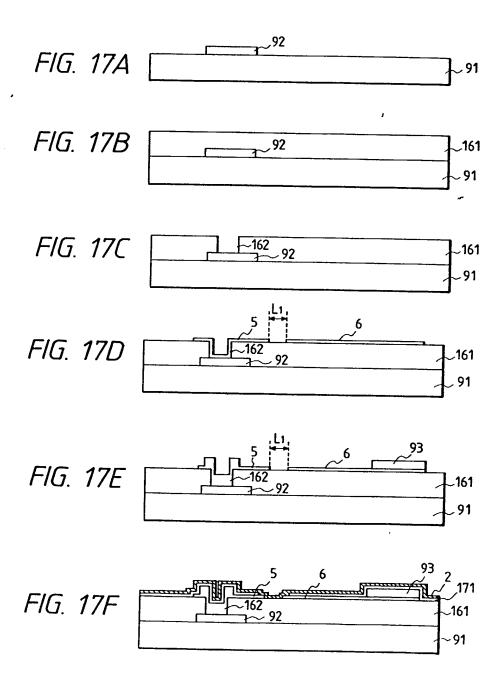


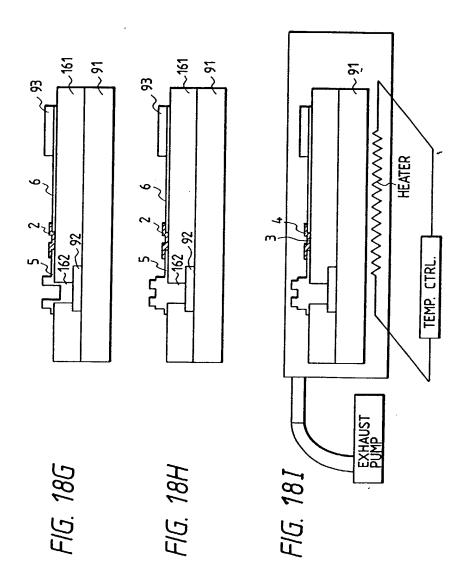


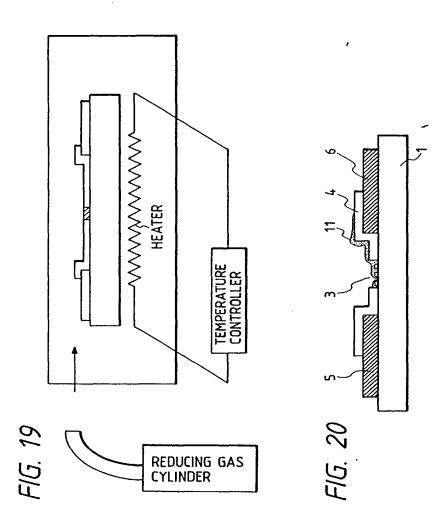




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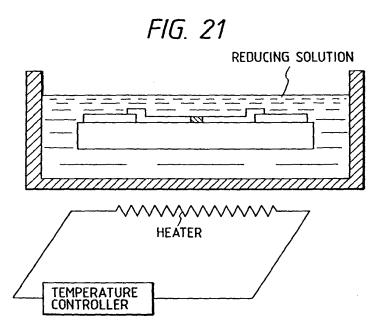
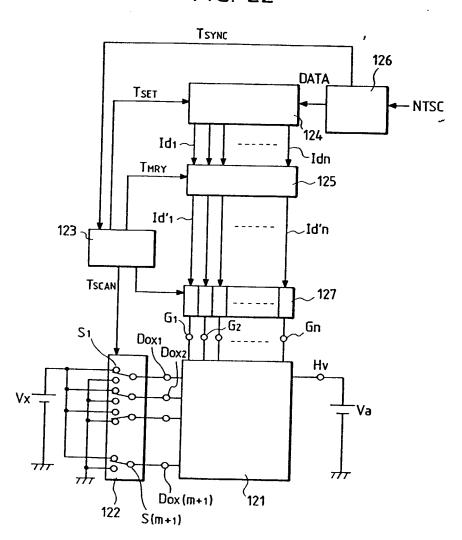


FIG. 22



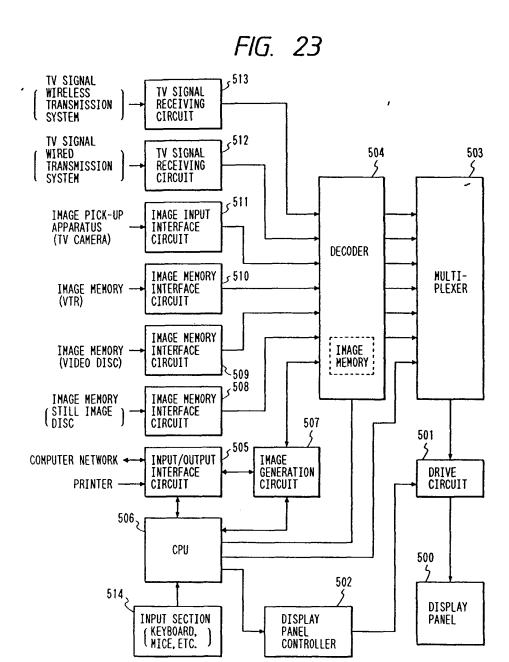


FIG. 24

